The Standardization of Volumetric Solutions

By

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Foreword

ORDINARILY, a standardized solution is a means to an end and not the end itself. Therefore, a set of good methods for preparing such solutions is very welcome. Analysts, research and other laboratory men have had training in these methods but when they wish to make up a solution, they do not like to spend much time in going through books and journals in order to find the directions for making up the specific one desired. In this book, the author has gathered together methods which have stood the test of laboratory experience, and has described them in a concise manner all ready for rapid laboratory use.

This book is not for the beginner, since it presupposes a general knowledge and practice of analytical chemistry. It is a handy reference work for the man who must hurry to get his results. The discussions of the methods and their good and bad points are short and very useful, and the text is replete with helpful hints, equations, tables of important data, expressions for calculating normalities, etc.

The writer believes that his friend and former asso-

ciate has done his self-appointed task well. His long experience in his chosen field gives him the proper background for such a work and this compilation of good practical methods ought to be of real service.

HARRY L. FISHER

Acknowledgment

The author wishes to express his thanks to Dr. Harry L. Fisher, U. S. Industrial Alcohol Co., V. L. Burger, General Laboratories, United States Rubber Products Co., and J. B. Lewis, Esso Laboratories, Standard Oil Co. of New Jersey, all of whom contributed helpful criticisms and suggestions.

R. B. Bradstreet

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CHAPTER I

General Consideration: *Definition of a Normal Solution. Normality and Equivalent Weight. Effect of Temperature and Buoyancy Error. Requirements for Standard Solutions. Calculations. Requirements of an Indicator.*

A NORMAL solution may be defined as a solution of known concentration, a liter of which is equivalent to a gram-atom of hydrogen. A fractional normal solution contains a fractional gram-atom of hydrogen per liter. The equivalent weight is the weight in grams corresponding to one gram-atom of hydrogen. In acid-base reactions, the hydrogen equivalent is easily found, since it is the number of titratable hydrogen atoms, thus:

$$
\begin{array}{ll}
(1) & NaOH + HCl \longrightarrow NaCl + H_2O \\
(2) & 2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O \\
(3) & Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O \\
(4) & 3NaOH + H_3PO_4 \longrightarrow Na_3PO_4 + 3H_2O
\end{array}
$$

The equivalent weight of either NaOH or HCl in (1) is the mol weight, that is, one mol of NaOH is equivalent to one mol of HCl. In (2), two mols of NaOH are equivalent to one mol of H_2SO_4, and the

equivalent weight of H_2SO_4 will be the molecular weight divided by 2, since the number of replaceable hydrogen atoms is 2, and a normal solution will contain this weight of H_2SO_4 in a liter of water. Equation (3) shows that 2 HCl are equivalent to 1 $Ca(OH)_2$. Calcium hydroxide is dibasic, and therefore has the equivalent of two replaceable hydrogens. Hence, the equivalent reacting weight will be the molecular weight divided by two. In case (4), by inspection it will be seen that there will be three replaceable hydrogen atoms (if all are titrated) and that the equivalent reacting weight will be the molecular weight divided by three.

In dealing with oxidation-reduction equations, the reacting weight (or equivalent weight) of a substance is the weight of substance equivalent to one half mol of oxygen (one half mol of oxygen is equivalent to one mol of hydrogen). Since oxidation-reduction is really electron transfer, it is simpler to determine the change of valence from the equation involved. The molecular weight divided by the change in valence is the equivalent reacting weight, and this weight made up to one liter is equivalent to one gram atom of hydrogen, or one half gram atom of oxygen.

This may be illustrated more clearly, perhaps, by the following examples:

$$(1)\quad MnO_4^- + 8\,H^+ + 5\,e \longrightarrow Mn^{++} + 4\,H_2O$$
$$(2)\quad MnO_4^- + 4\,H^+ + 3\,e \longrightarrow MnO_2 + 2\,H_2O$$

In the first equation, manganese, as a permanganate, with a valence of 7, has been reduced to a manganous salt having a valence of 2, or, in other words, there has been a transfer of 5 electrons. This reaction takes place in acid solution and the equivalent weight, therefore, is $\frac{MnO_4^-}{5}$

Equation (2) represents oxidation with alkaline permanganate, and by inspection it is found that the valence change is 3. Consequently, there has been an electron transfer of 3, and the equivalent weight is $\frac{MnO_4^-}{3}$.

$$(3)\quad Cr_2O_7^{--} + 14\ H^+ + 6\ e \longrightarrow 2\ Cr^{+++} + 7\ H_2O$$
$$(4)\quad 2\ S_2O_3^{--} + I_2 + 2\ e \longrightarrow S_4O_6^{--} + 2\ I^-$$

Example (3) illustrates dichromate oxidation, which involves a transfer of 6 electrons, and gives a reacting weight equal to $\frac{Cr_2O_7^{--}}{6}$. In the last equation (4), the iodine has been reduced from zero valence to a valence of minus 1, and therefore, the equivalent weight will be $\frac{I}{1}$.

Since oxidation is the result of a loss of electrons, and reduction represents a gain of electrons, it is not necessarily true that an oxidizing agent always contains oxygen [as for instance iodine in equation (4)]. Equations (1) and (2) show that the equivalent reacting weight of an oxidizing agent may vary depending upon the medium in which the reaction takes place.

The equivalent weights of precipitation reagents may

be likewise determined from their reactions. For instance:

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

By inspection, it is seen that one mol of silver nitrate reacts with one mol of sodium chloride to form one mol of silver chloride. Therefore, their equivalent reacting weights in this case are their molecular weights.

Standard solutions, in some cases, may be prepared without further standardization where the substance is known to be pure, and does not change appreciably due to atmospheric conditions. Potassium dichromate, potassium iodate, oxalic acid, and silver nitrate are a few examples. However, it is always desirable to standardize a solution. It is good practice to weigh the substance as accurately as possible, to avoid the necessity later of diluting to the proper normality. Also, it is advisable to weigh slightly more than the theoretical amount, since it is easier to dilute than to raise to the desired normality. The dilution may be calculated as follows (contraction of the solution being neglected, as usually no great error is involved):

Let V = volume of solution before dilution
V_1 = volume of solution after dilution
N = normality of solution before dilution
N_1 = normality desired after dilution

Then $NV = N_1V_1$

or $V_1 = \frac{NV}{N_1}$

and $V_1 - V = x$ cc of solvent to be added to the original volume.

Solutions as dilute as tenth normal are affected but little by temperature changes,[1,2,3] but with half normal and normal solutions, the temperature should be considered. The following table, after W. Schloesser,[2] gives a partial list of corrections to be applied to standard solutions referred to 20° C as a standard temperature.

T°C	Water 0.01*N* Solutions 0.1*N* HCl	0.1*N* Solutions	0.5*N* HCl	1.0*N* HCl	0.5*N* NaOH	1.0*N* NaOH
15	+0.8	+0.9	+0.9	+1.0	+1.1	+1.3
16	0.6	0.7	0.8	0.8	0.9	1.1
17	0.5	0.6	0.6	0.6	0.7	0.8
18	0.3	0.4	0.4	0.4	0.5	0.6
19	0.2	0.2	0.2	0.2	0.2	0.3
20	0.0	0.0	0.0	0.0	0.0	0.0
21	—0.2	—0.2	—0.2	—0.2	—0.2	—0.3
22	0.4	0.4	0.4	0.5	0.5	0.6
23	0.6	0.6	0.7	0.7	0.8	0.9
24	0.8	0.9	0.9	1.0	1.0	1.2
25	1.0	1.1	1.1	1.2	1.3	1.5

Schloesser assumes the coefficient of cubical expansion of glass to be 0.000027.

Certain precautions should be observed regarding standard solutions. It is good policy to store all standard solutions in the dark, where there is a minimum of temperature variation, and where the containers cannot be contaminated with dust or organic material. Solutions should be labelled in the following manner:

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[1] Yokichi Osaka, *J. Tokyo Chem. Soc.* **40,** 424 (1919); *Chemical Abstracts* **14,** 159 (1920).

[2] W. Schloesser, *Chem. Ztg.* **29,** 510 (1905).

[3] N. Schoorl, *Chem. Weekblad* **23,** 581 (1926).

Name and formula
Normality or factor
Name and notebook reference of the person making up and standardizing the solution
Temperature of standardization
Date of standardization

This information makes it easier to check any possible errors in standardization. It is also advisable to record the equivalent weight, to facilitate preparation of subsequent solutions. Solutions that have stood for a considerable time,[4] and particularly those that show a tendency to deteriorate quickly, should always be restandardized before using.

Usually, in the preparation of standard solutions, the theoretical amount of substance is weighed in air against brass weights, neglecting the effect of buoyancy. Since atomic weights and, it follows, molecular weights are calculated to vacuo, there is, therefore, an error introduced when weighings are made in air. The magnitude of this error is such that it may be neglected. The equivalent weights found in the following pages are not corrected to vacuo.

Archimedes' principle states that bodies immersed in a fluid are buoyed up by a force equal to the weight of the displaced fluid. This law holds for gases as well as for liquids.

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[4] J. Linder, *Mikrochemie,* Festschr. von Hans Molisch, 301–13 (1936).

If a mass of brass is weighed against brass weights, the buoyancy force on both sides of the balance is the same, provided the volume is the same, and no correction need be made. If, however, the density of the weights is greater than that of the substance being weighed, the apparent weight of the substance in air will be less than its true weight in vacuo. The weight reduced to vacuo may be calculated from the following formula:

$$w = W + W\delta\left(\frac{1}{d} - \frac{1}{d_1}\right)$$

where W = true weight
w = apparent weight in air
δ = density of air
d = density of substance being weighed
d_1 = density of weights used

Density of brass is 8.4, and density of air is 0.0012.

Since the majority of commonly used standard solutions cannot be prepared by direct weighing of the substance in question, some means must be taken to establish the exact value of the solution. Any errors in standardization will be recurrent in all subsequent determinations made with the solution. In the first place, therefore, some substance of known purity must be available for evaluating the solution. Certain requirements are necessary for a primary standard. It should have a high equivalent weight, be easily obtainable pure, or easily purified. It should be neither hygroscopic nor efflorescent.

It is obvious that the primary substance must bear a stoichiometrical relation to the standard solution.

In the actual standardization, several other points must be observed. In weighing out the primary standard, it must be remembered that, in general, the accuracy of an analytical balance is ± 0.1 mg, so that sufficient sample must be weighed to reduce this error to a minimum. This, in effect, is an argument for the use of substances having a high equivalent weight. The actual titration should fall within the limits of the burette, that is, it should not titrate over 50 cc. No less than 40 cc should be used. The errors involved in titration, while small, are cumulative, (reading, drainage, and error in the end point—plus or minus one drop). If the end point is overrun, say, by one drop, then the error involved here is about ± 0.03 cc, since this is approximately the volume of one drop from a fine-tipped burette. If, now, the remaining errors of reading and drainage are added to this, it is easily seen that at least 40 cc must be used in order to keep the errors within 0.1–0.2 per cent. Since the accuracy of standardization is between 0.1 and 0.2 per cent, it will be understandable that every precaution must be taken. Standardizations, involving a back titration with another standard solution, are open to further errors which may be additive, since they involve an additional titration. At least three checks should be made on any standardization. They should check within 0.2 per cent. Care-

fulness cannot be too highly stressed in the standardization of a reagent, since the accuracy of future determinations depends upon the accuracy with which the value of the standard solution was determined.

The calculations involved in volumetric standardizations are very simple. Normality may be calculated according to the following formula.

$$\text{Normality} = \frac{\text{weight of standard substance}}{\text{milliequivalent of std. x cc titration}}$$

The milliequivalent may be defined as the weight of standard substance contained in one cubic centimeter of a normal solution of that standard substance. The milliequivalent multiplied by the number of cubic centimeters used for titration gives the weight in grams of standard substance. The weight of standard substance divided by this gives the ratio of the standard solution to the theoretical normal solution. In other words, if the normality found is 0.1050 normal, it means simply that one cubic centimeter of the solution contains 1.050 times as much as the theoretical amount.

In the choice of a suitable indicator, the field is so large that it may, in many cases, be left to the discretion of the operator. There are, however, certain requirements to be met, namely, an indicator whose transition range is within the range of the reaction involved, and a color change which is sharp enough to be differentiated by the analyst.

The point at which the indicator changes color is taken as the end point, meaning that at this point, an equivalent amount of standard reagent has been added. Strictly speaking, this may or may not be the exact end point or equivalence point. This can be determined by electrometric titration, the difference in the two titrations being known as the titration error.

Most indicators are organic, and are either weak acids or weak bases. They are slightly ionized, according to the following:

$$HI \leftrightarrows [H]^+ + [I]^- \text{ (Acids)}$$
$$IOH \leftrightarrows [I]^+ + [OH]^- \text{ (Bases)}$$

Oxidation and reduction indicators depend for their color changes on oxidation or reduction of themselves. In some cases, the reagent itself acts as its own indicator.

A recent class of indicators, known as adsorption indicators,[5] has been used with more or less success in the determination of halides and sulphates. In general, they are not applicable to standardizations, although they have been used[6] in acidimetry and alkalimetry. A theoretical discussion of various types of indicators will be found in Kolthoff and Furman, *Volumetric Analysis, Vol. I* (1928), 82.

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[5] A. R. Ubbelohde, *Chem. Rev.* 16, 53 (1935).

[6] Sachindra Nath Roy, *J. Indian Chem. Soc.* 14, 120 (1937); see also *Chemical Abstracts* 31, 5293 (1937); *Chemical Abstracts* 30, 8064 (1936).

CHAPTER II

Calibration of Volumetric Apparatus

SINCE volumetric procedures require accurate measurement of volume, the importance of knowing the exact volumes of the various apparatus used cannot be overlooked. The simplest and most obvious solution to this problem, wherever possible, is to use apparatus calibrated by the U. S. Bureau of Standards. Apparatus calibrated by the Bureau is always accompanied by a table of volume corrections over a range of working temperatures. This, however, is comparatively expensive, and it is easy enough to purchase a good grade of glassware that falls within the limits of tolerance allowed by the Bureau of Standards, and calibrate it in the laboratory. It is never advisable to rely on the accuracy of a piece of apparatus without first calibrating it.[1]

In the process of standardization, volumetric flasks, pipettes, and burettes are necessary. Volumetric flasks are graduated to *contain* a definite volume, and pipettes

[1] *Bur. Standards Circ. No. 9* (1916).

and burettes to *deliver* a definite volume. Before any attempt is made to calibrate apparatus, it must be thoroughly cleaned. This is done by rinsing with tap water, filling with fresh chromic acid, and letting stand for several hours. After this treatment, the chromic acid is withdrawn, and the apparatus washed free from the acid with tap water. It is now washed with distilled water and drained. If the water does not appear to wet the inside of the apparatus evenly, several washes with acetone, and then distilled water may be efficacious. If this does not have any effect, another treatment with chromic acid will be necessary.

Since the calibration is made with water, it is not necessary to dry the apparatus. All volumetric apparatus are calibrated to contain or deliver a definite volume at a standard temperature, usually taken at 20° C. This means, of course, that at this temperature, the apparatus will contain the designated volume. At any other temperature, the volume will vary depending upon the expansion of the glass and the density of water. Buoyancy effect is also taken into consideration, using 0.0012 gm per cc, the density of air (not strictly correct, because this figure will vary slightly depending upon temperature, humidity and pressure), as sufficiently accurate for all calibrations.

Usually, the temperature at the time of calibration is not 20° C, so that all weighings are made under existing conditions and referred back to 20° C. The

liter is the unit of volume in the metric system, and is the volume of a mass of one kilogram of water at maximum density.

Calibration of Flasks

Fill the flask to the graduation on the neck with distilled water at room temperature and weigh. This weight is reduced to vacuo (mass), according to the formula:

$$w = W + W\delta\left(\frac{1}{d} - \frac{1}{d_1}\right) \quad \text{(See Chapter I)}$$

The volume at room temperature is this mass divided by the density of water at room temperature.

$$\text{Volume at R. T.} = \frac{\text{Mass}}{dH_2O}$$

This gives the volume of the flask at room temperature. It is now necessary to calculate this volume to 20° C, and this may be done by applying the following:

$$V_T = V_{T_1} + 0.000025\, V_{T_1}(T - T_1)$$

Where V_T = Volume at standard temperature
V_{T_1} = Volume at calibration temperature
T = Standard Temperature
T_1 = Calibration Temperature

Coefficient of cubical expansion of glass* = 0.000025

* Coefficient of cubical expansion of Pyrex glass is 0.00000032 or less, between 19 and 350° C.

Calibration of Pipettes

After cleaning the pipette, immerse the tip in water, fill to the mark, discard and fill again exactly to the graduation. Wipe any excess water from the pipette by means of a soft rag and transfer the contents to a tared and stoppered Erlenmeyer flask, allowing the pipette to remain vertical until discharged and then touching the tip to the side of the flask and allowing it to remain for fifteen seconds. Do not blow out the pipette. Reweigh the Erlenmeyer flask and calculate the volume in the same manner as for volumetric flasks.

Calibration of Burettes

The calibration of a burette may be carried out in two ways: 1. Measure 5 cc of water from the burette into a tared and stoppered 100 cc Erlenmeyer flask and weigh. Record the weight. Add 5 cc more to the flask and reweigh. Repeat this process until the capacity of the burette has been measured into the flask and weighed. 2. Measure 5 cc from the burette and weigh. Refill the burette and measure 10 cc into a flask and weigh. Repeat this procedure until the last weighing represents the capacity of the burette. The calculations are the same as for flasks and pipettes. The difference between the true volume and the observed volume is the correction to be applied in a titration. A curve may

be plotted to show the correction and true volume at any point.

When reading the volume, care must be taken to avoid parallax. In the case of pipettes and flasks or any piece of apparatus on which the graduation extends around the circumference, this is avoided, but with burettes, a possible error may occur if the graduation and the eye are not in the same horizontal plane. The error may be either positive or negative. This may be overcome by using a strip of paper having a straight edge, bringing it to the bottom of the meniscus and lining up both sides.

The method of calibration herein described is probably the most common one. Another means of calibration is by the use of Morse-Blalock [2] bulbs, which, however, require a more complicated set-up, and are generally not available in most analytical laboratories.

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[2] Morse and Blalock, *Am. Chem. J.* 16, 479 (1894).

CHAPTER III

Indicators: *Definition, Classification, Classification of Reaction, Acid-Base Indicators, Oxidation-Reduction Indicators, Indicators for Precipitation Reactions. General Discussion.*

ANY compound in solution exhibiting a color change or producing a precipitate, by addition of an excess of one of the reactants, may be considered as an indicator. In other words, an indicator produces a visual change at, or near, the equivalence point. It may be a separate compound or one of the reagents, as in the case of permanganate or iodine.

Indicators may be divided roughly into three classes:

1. acid-base
2. oxidation-reduction
3. precipitation

For an extended survey of indicators, and theoretical considerations, reference should be made to the many excellent books on this subject.[1, 2, 3, 4]

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[1] Kolthoff and Furman, *Indicators* (Wiley).

[2] Kolthoff and Furman, *Volumetric Analysis, Vol. I & II* (Wiley, 1929).

[3] Clark, *Determination of Hydrogen Ions* (Williams & Wilkins).

[4] Hubert T. S. Britton, *Hydrogen Ions* (Van Nostrand).

Acid-Base Indicators

The color change exhibited by indicators is produced by a change in H^+ concentration, and the range through which this occurs is called the transition interval. Most acid-base indicators are weak organic acids or bases which give one color when undissociated (pseudo form) and another when ionized (ionogen). Since they are weak acids or bases, the mass action law applies, and it is obvious, therefore, that the indicator change is a function of the H^+ concentration.

Thus, if $HI \rightleftarrows [H^+] + [I^-]$

then, $K_{Ind.} = \dfrac{[H^+] \times [I^-]}{HI}$

Transposing, $K_{Ind.} \times HI = [H^+] \times [I^-]$

or $\dfrac{K_{Ind.}}{[H^+]} = \dfrac{[I^-]}{HI}$, so that when

$K_{Ind.} = [H^+]$, $[I^-] = HI$,

and the indicator is half changed over. At any pH, then, the equilibrium constant holds, and at any particular instant, there are present both acid and basic phases. At some point, however, either one will be in sufficient concentration to cause a visual change of color.

This change, for the most part, is not sudden, but covers from one to several pH units. This is due,

mainly, to the inability of the eye to gauge the color change accurately.

The transition range, obviously, has an upper and lower limit, at one end of which, the acid form predominates, whereas the other is alkaline.

If, for instance, 10% of the alkaline form of an indicator is sufficient to produce a visible change in the presence of the acid form, then,

$$\frac{K_{Ind.}}{[H^+]} = \frac{[I^-]}{HI} = \frac{1}{10}, \text{ and}$$

$$[H^+] = K_{Ind.} \times 10$$

Expressing this as a logarithmic function,

$$pH = pK_{Ind.} + 1$$

Now, conversely, if it is assumed that 10% of the acid form is enough to cause a color change in the presence of 90% of the alkaline form, then,

$$\frac{K_{Ind.}}{[H^+]} = \frac{[I^-]}{HI} = \frac{10}{1}$$

$$\text{or} \quad [H^+] = \frac{K_{Ind.}}{10}$$

$$\text{or} \quad pH = pK_{Ind.} - 1$$

The transition interval, therefore, is equivalent to 2 pH units.

The majority of indicators is affected by any great

change in temperature. Salt error, however, may be neglected, unless the concentration is very high. It tends to affect the equilibrium and the color change of the indicator, due to the difference in absorption of light.

A large variety of indicators is available for acid-base titrations, and a suitable choice is dependent upon the classification of the reaction, that is:

1. strong acid-strong base
2. weak acid-strong base
3. strong acid-weak base
4. weak acid-weak base

Each case will be considered separately.

1. Strong acid-strong base. In this case, it may be assumed that both are completely ionized, and if the base is as strongly ionized as the acid, complete neutrality is indicated. Since the definition of a neutral solution is one in which the $[H^+]$ and $[OH^-]$ concentrations are both 10^{-7}, then for this type of neutralization, an indicator having a transition range around pH 7 is acceptable.

2. Weak acid-strong base. If an acid is less strongly ionized than the base used in the titration, equilibrium will be attained in a basic solution. This conclusion is obvious, when it is realized that two conditions must be fulfilled: first, that the ionization constant of the acid must be satisfied, and second, that $C_H \times C_{OH} = 10^{-14}$ (actually 1.2×10^{-14}) will be maintained. At equilib-

rium, there must be unionized acid present. This lowers the concentration of $[H^+]$ and leaves free $[OH^-]$ in the solution. The pH of the solution, at equilibrium, will be greater than 7, hence, an indicator having a range greater than pH 7 must be used.

3. Strong acid-weak base. If the conditions stated under 2 are reversed, it will be seen that equilibrium will take place in acid solution. In this case, an indicator having a pH of less than 7 should be used.

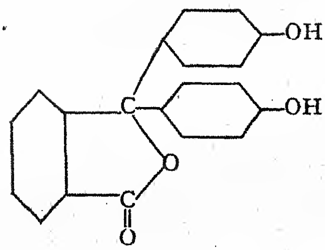
4. Weak acid-weak base. In this case, three equilibrium constants must be satisfied, namely, ionization constants of both acid and base, and ionization constant of the water formed by the reaction. If the acid and base are ionized to about the same degree, e.g. acetic acid and ammonia, then the resulting solution will have a pH of 7. If one is more strongly ionized than the other, the same conditions will exist as stated previously in cases 2 and 3, and the same kind of indicators chosen.

The following represent a few of the indicators most commonly used in acid-base reactions. They cover a wide range of pH.

Phenolphthalein

Type: Belongs to the phthaleïn group.

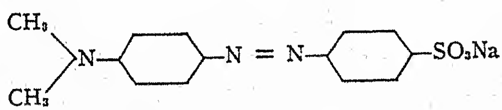
Structural formula:



pH range 8.3–10.0. Color change from colorless to red violet.

Methyl Orange (sodium dimethylamino azobenzene sulphonate)

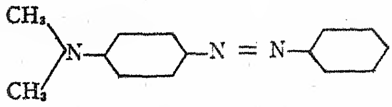
Type: Belongs to the azo group.
Structural formula:



pH range 2.9–4.5. Color change from orange red to orange yellow. Although this indicator is widely used, the color change is not as sharp as could be desired, and it may be replaced, for instance, by methyl yellow. The color change for this indicator is much sharper. Methyl orange is not affected by carbon dioxide.

Methyl Yellow (dimethylamino azobenzene)

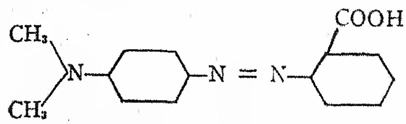
Type: Belongs to the azo group.
Structural formula:



pH range 2.9–4.0. Color change from red to yellow. (Not affected by CO_2).

Methyl Red (dimethylamino azobenzoic acid)

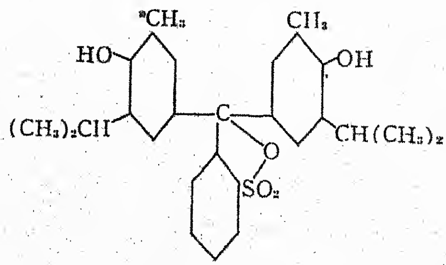
Type: Belongs to the azo group.
Structural formula:



pH range 4.2–6.3. Color change from red to yellow.

Thymol Blue (thymol sulphon phthalein)

Type: Belongs to the phthalein group.
Structural formula:



pH range: Acid 1.2–2.8
alkaline 8.0–9.6.

Color change in the acid range from red to yellow, and yellow to blue in the alkaline range.

Oxidation-Reduction Indicators

Any system in which there is a change of valence may be classified as an oxidation-reduction reaction. Therefore, when an atom or complex ion is oxidized, its positive valence is increased, or its negative valence is decreased, and the converse is also true of reduction. In other words, a substance which is oxidized gives up electrons, and a substance which is reduced adds electrons.

Previously, the use of outside indicators was more or less universal for determining the end point. If colorless solutions are to be titrated, it is possible for the reagent to act as its own indicator, for instance, potassium permanganate, ceric sulphate, and iodine.

Internal oxidation-reduction indicators have been applied to dichromate, permanganate, ceric sulphate, and ferrocyanide titrations. An oxidation-reduction indicator should, of course, be reversible, otherwise its use is limited. For every oxidation-reduction equation, there can be calculated a definite electrode potential using the Nernst equation.[5]

$$E = \frac{RT}{nF} \text{Ln} \frac{p}{P},$$

[5] Engelder, *Calculations of Qualitative Analysis*, Chapter IX, p. 131.

which can be simplified to

$$E = \frac{0.059}{n} \log \frac{C}{k}$$

or

$$E = \frac{0.059}{n} \log C + \frac{0.059}{n} \log \frac{1}{k}$$

If the concentration is one molar, then

$$E = \frac{0.059}{n} \log \frac{1}{k}$$

or

$$E = E_0$$

E_0 is the oxidation potential at molar concentration and is a constant for each system, so that the oxidation potential may be calculated for any mixture, from the following equation:

$$E = E_0 + \frac{0.059}{n} \log \frac{C_{oxd}}{C_{red}}$$

where C_{oxd} is the concentration of the oxidized ion, and C_{red}, the concentration of the ion in reduced form.

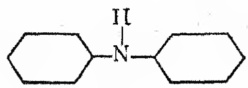
The selection of a suitable indicator is based on the normal potentials of both indicator and the oxidizing-reducing system in question, since the specific action of the indicator is dependent upon its electrode potential. Therefore, any indicator, having a lower oxidation potential than the system in which it is used, will exhibit a color change. There must not, however, be a very

large difference. If this is the case, the oxidation potential (of the system) should be reduced, and this is accomplished in some cases by forming complex ions.

The following indicators have been used successfully in oxidation-reduction reactions.

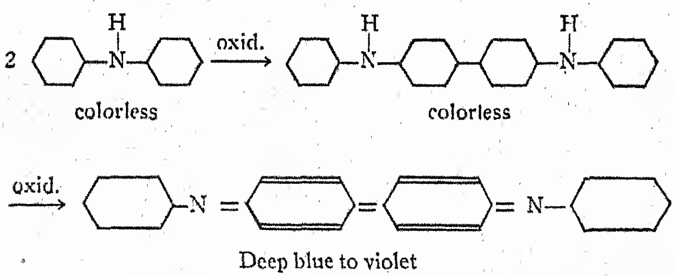
Diphenylamine

Structural formula:



Oxidation potential: –0.76 volts.

The first step in the oxidation of this indicator is to diphenylbenzidine, and thence to colored compound



Color change is colorless to deep blue or violet. Since some of the reagent goes to complete the oxidation of the indicator, it is necessary to make a correction [6] for the amount used.

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[6] W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* **49**, 356 (1927).

Diphenylbenzidine

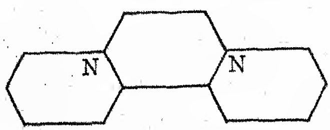
Structural formula:

Oxidation potential: –0.76 volts.

Color change is from colorless to deep blue or violet. The oxidation proceeds as above. The blue compound is stable for only a short while in the presence of oxidizing agents.

Ortho-Phenanthroline Complex[7]

Oxidation potential is –1.14 volts. The usual form of this indicator is the ferrous ion complex. The structural formula of *o*-phenanthroline is:



It dissolves in solutions of ferrous salts, three molecules combining with one ferrous ion.

Color change is from red to blue.

Starch Solution[8, 9]

The preparation of starch solution is more difficult

[7] *Ortho-phenanthroline,* monograph published by The G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio.

[8] C. L. Alsberg and E. P. Griffing, *J. Am. Chem. Soc.* 53, 1401 (1931).

[9] C. L. Alsberg and E. P. Griffing, *J. Am. Chem. Soc.* 48, 1299 (1926).

than is ordinarily supposed. A solution which will prove satisfactory over a long period can be prepared [10] in the following manner: Mix 0.5 gm of potato starch with 2.5 cc of water and pour into 200 cc of boiling water, stirring meanwhile. Boil fifteen minutes. Cover the flask or beaker with a watch glass to prevent scum forming by evaporation during boiling. The final solution should not contain any suspended matter. If this is kept covered and allowed to stand on a steam plate, the solution will keep indefinitely. If heating is impossible, 0.25 gm of salicylic acid may be added as a preservative. With this addition, starch solutions have given good end points after a year, although considerable sediment had formed, and only the supernatant liquid was used.

The condition of starch, as received from supply houses, is somewhat uncertain. Sometimes fresh starch contains dextrin, which gives a reddish violet color, and is not immediately discharged by thiosulphate. Starch of this sort should be discarded. The color change is from colorless to blue. In the presence of iodide, the sensitivity is of the order of 2×10^{-5} concentration of iodine. Heat decreases the sensitivity, as does alcohol.

Indicators for Precipitation Reactions

In precipitation reactions, application of the differences in solubility is made. To take a concrete example,

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[10] M. Starr Nichols, *J. Ind. Eng. Chem., Anal. Ed.* 1, 215 (1929).

the reason that potassium chromate can be used as an indicator in the standardization of silver nitrate with sodium chloride may be explained in the following manner: The solubility of silver chloride is extremely small and that of silver chromate relatively large, so that no silver chromate will be formed until all chloride ions have been precipitated. Ferric alum acts in a similar manner in the silver nitrate-ammonium thiocyanate reaction.

General Discussion

The short list of indicators already described should in no way be taken as representative of indicators as a whole. They are discussed only from the standpoint of their usefulness in standardization of normal solutions. Some indicators such as thymol blue and 4-nitrocatechol [11] exhibit three color changes, representing two transition intervals, one in the acid range, and one in the alkaline. Often, two indicators are mixed [12, 13, 14] to give a transition range between certain pH values.

New oxidation-reduction indicators are constantly being prepared and tested. It has been found that the

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[11] S. R. Cooper and V. J. Tulane, *J. Ind. Eng. Chem., Anal. Ed* 8, 210 (1936).

[12] H. A. J. Pieters, *Chem. Weekblad* 32, 539.

[13] Kurt Hoppner, *Deut. Zuckerind.* 61, 361 (1936).

[14] Kolthoff and Furman, *Volumetric Analysis, Vol. II* (1929), p. 64.

sodium or barium salt of diphenylamine sulphonic acid [15] is a suitable oxidation-reduction indicator, particularly in presence of tungstates. In this respect, it is better than either diphenylamine or diphenylbenzidine, since tungstates interfere with these indicators.

Phenylanthranilic acid,[16, 17] para and meta tolylphenylamine, and naphthidine [18] have been proposed and used.

There is little to be said regarding adsorption indicators, as they are seldom used in procedures ~~for stand-~~ ardizations. Fluorescein and eosin have been known and used for some time in the determination of halogens as the silver halides. Sodium rhodizonate [19, 20] (sodium salt of tetrahydroxy quinone) is being used as an internal indicator for the determination of sulphates volumetrically. In the use of these indicators, there is a tendency toward an indicator lag, particularly in solutions of fairly high concentrations.

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[15] L. A. Sarver and I. M. Kolthoff, *J. Am. Chem. Soc.* **53,** 2902, 2906 (1931).

[16] A. U. Kirsanav and U. M. Cherkasou, *Zavodskaya Lab.* **5,** 143; *Bull. Soc. Chim. (5)*, **3,** 817.

[17] V. S. Svirokomskii and V. V. Stepin, *J. Am. Chem. Soc.* **58,** 928 (1936).

[18] Leora E. Straka with R. E. Oesper, *J. Ind. Eng. Chem., Anal. Ed.* **6,** 465 (1934).

[19] Mutschin and Pollak, *Z. Anal. Chem.* **108,** 8 (1937).

[20] Mutschin and Pollak, *Z. Anal. Chem.* **108,** 309 (1937).

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Chromotropic Acid as an Indicator in Fluorescence—Volumetric Analysis, Kocsis and Nagy, *Z. Anal. Chem.* **108**, 317 (1937).

Indicators, I. M. Kolthoff, *J. Ind. Eng. Chem., Anal. Ed.* **8**, 237 (1936).

Diphenylcarbazide, An Internal Indicator for Use in the Titration of Iron with Dichromate, H. E. Crossley, *Analyst,* **61**, 164.

Internal Indicator for Dichromate-Titration of Iron, M. E. Weeks, *J. Ind. Eng. Chem., Anal. Ed.* **4**, 127 (1932).

Oxidation-Reduction Indicators for Use with Dichromate II, Stuart Cohen and Ralph E. Oesper, *J. Ind. Eng. Chem., Anal. Ed.* **8**, 364 (1936).

A Better Titrating Solution Using Diphenylamine Indicator, W. K. Gibson, *Chemist-Analyst* **26**, 28 (1937).

Indicator: Ferrous-ortho-phenanthroline, Walden, Hammet, and Chapman, *J. Am. Chem. Soc.* **53**, 3908 (1931).

Starch Indicator, Fales, *Inorganic Quantitative Analysis* (The Century Co., New York, 1925), 300.

The Constitution of Starch Iodide, A. Lottermoser, *Z. Angew. Chem.* **34**, Aufsatzteil, 427 (1921); *Chemical Abstracts* **16**, 10 (1922).

The Taking Up of Iodine by Various Substances, A. Lottermoser, *Kolloid Z.* **33**, 271 (1923); *Chemical Abstracts* **18**, 925 (1924).

Starch Iodide, A. Lottermoser, *Z. Angew. Chem.* **37**, 84 (1924); *Chemical Abstracts* **18**, 950 (1924).

CHAPTER IV

Standard Substances

If the concentration of a solution is to be determined accurately, it is necessary to compare it with some substance of known purity. Not all substances are suitable for standards, and, because of this fact, certain requirements are necessary, chief among which are high equivalent weight, stability at ordinary temperatures, ease of purification, solubility and absence of side reactions. The substance should neither deliquesce nor effloresce.

Many attempts have been made to prepare a universal primary standard, but, so far, such work has not been successful. There are, however, many excellent primary standards available. Some of these overlap, that is to say, they may be used as a standard for more than one type of standard reaction. They may be placed in general classifications as follows:

1. Standard substances for acids and bases
2. Standard substances for precipitation reagents
3. Standard substances for oxidation-reduction reagents

Considering the first class of standards, they may be further subdivided into those suitable for acids and those suitable for bases. In the first category falls anhydrous sodium carbonate, the classical primary standard for acids. In spite of the recognized shortcomings, it has stood the test of time. Extreme care, however, must be exercised in using it, both in preparation and in standardization. Smith and Croad[1] have found that it is not safe to heat the bicarbonate above 300° C in preparing the carbonate, as there is appreciable decomposition at 310–315° C. Sodium carbonate suitable for standardization purposes, according to Stalony-Dobrzanski,[2] is obtained by heating sodium bicarbonate between 150 and 280° C. Decomposition of the sodium bicarbonate is completed after 100 minutes. There is also a disadvantage of low equivalent weight and the fact that it is hygroscopic.

Borax, originally used in the anhydrous state, was unsatisfactory due to the difficulty in preparing and keeping the anhydrous salt. The decahydrate,[3,4,5] how-

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[1] G. F. Smith and G. F. Croad, *Ind. Eng. Chem., Anal. Ed.* **9**, 141 (1937).

[2] J. Stalony-Dobrzanski, *Roczniki Chem.* **14**, 1106 (1934).

[3] G. Kilde, *Dansk. Tids. Farm.* **10**, 273 (1936), (English summary).

[4] F. H. Hurley, Jr., *Ind. Eng. Chem., Anal. Ed.* **8**, 220 (1936).

[5] F. H. Hurley, Jr., *Ind. Eng. Chem., Anal. Ed.* **9**, 237 (1937).

ever, makes a suitable standard which possesses the advantage of a high equivalent weight.

Carlton [6] proposed the use of symmetrical diphenyl guanidine, but a comparison made by Thornton and Christ [7] showed that the results obtained were low and suggested that a better method of purification was necessary if it was to be used as a standard. On the other hand, Young [8] states that it may be purified simply by recrystallization to provide a satisfactory primary standard. Guanidine carbonate,[9] prepared from calcium cyanide, is very pure, contains no water of crystallization, and is not hygroscopic. It behaves as a monoacidic base and is accurate enough for use as a standard in routine work.

Potassium bicarbonate,[10, 11, 12, 13] as an acidimetric standard, is prepared by passing CO_2 into an alcoholic solution of potassium hydroxide. It is a reliable standard for all but very accurate work. Solutions stronger than $N/10$ show a tendency to evolve CO_2.

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[6] C. A. Carlton, *J. Am. Chem. Soc.* **44**, 1469 (1922).

[7] W. M. Thornton and C. L. Christ, *Ind. Eng. Chem., Anal. Ed.* **9**, 339 (1937).

[8] J. W. Young, *Can. J. Research* **17B**, 192 (1939).

[9] A. H. Dodd, *J. Soc. Chem. Ind.* **40**, 80–90 T (1921).

[10] L. W. Winkler, *Z. angew. Chem.* **28**, 264 (1915); *Chemical Abstracts* **9**, 2747 (1915).

[11] G. Incze, *Z. anal. Chem.* **54**, 585 (1916).

[12] G. Bruhns, *Chem. Ztg.* **41**, 386 (1917); *J. Chem. Soc.* **112**, II, 419.

[13] G. Bruhns, *Chem. Ztg.* **48**, 89 (1924).

Dipotassium periodate,[14] $K_2H_3IO_6 \cdot 3H_2O$, reacts quantitatively with strong acids in the following manner:

$$H_3IO_6^{--} + H^+ \longrightarrow IO_4^- + 2H_2O$$

It has the advantage of a relatively high equivalent weight. A sharp end point is obtained with methyl red as an indicator.

The use of thallous carbonate has been suggested by Hac and Kamen.[15] As a result of their experiments, they concluded that it was a satisfactory primary standard. Reproducible results, using methyl orange as an indicator, were obtained, which agreed within a few thousandths of 1%, and the values compared favorably to those resulting from the use of Na_2CO_3, $Na_2B_4O_7$ and $Na_2C_2O_4$. Work by Berry,[16] and Jensen and Nilssen [17] gives further proof of the suitability of thallous carbonate.

A method of great precision for the standardization of hydrochloric acid is the use of metallic silver [18] as

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[14] L. Malaprade, *Congr. chim. ind., Compt. rend. 18 ème Congr. Nancy Sept.-Oct.* (1938), 91.

[15] R. Hac and K. Kamen, *Collection Czechoslov. Chem. Commun.* 4, 145; *Chem. Listy* 26, 6 (1932); *Chemical Abstracts* 26, 3746 (1932).

[16] A. J. Berry, *Analyst*, 64, 27 (1939).

[17] Einar Jensen and Bailli Nilssen, *Ind. Eng. Chem., Anal. Ed.* 11, 508 (1939).

[18] C. W. Foulk and L. A. Pappenhagen, *Ind. Eng. Chem., Anal. Ed.* 6, 430 (1934).

an ultimate standard. It is a useful nephelometric method, and the results obtained exceed those of other methods in accuracy.

Another substance obtainable in a high degree of purity is yellow mercuric oxide.[19,20] It is not hygroscopic and contains no water of crystallization. The principle depends upon the following reaction:

$$HgO + 4\ KI + H_2O \longrightarrow K_2(HgI_4) + 2\ KOH$$

The mercuric oxide is dissolved in a large excess of potassium iodide (0.5 gm HgO and 7.5 gm KI), and the resulting potassium hydroxide is titrated with the acid to be standardized, using phenolphthalein as an indicator. Kolthoff and van Berk[21] observe that whereas results by this method are accurate to within 0.1%, the method is not as precise as standardization with borax. Lazarkevich[22] confirms this and states that mercuric oxide should be used only for rough work.

A report by Vandaveer[23] on the standardization of acidimetric solutions compares the results obtained by

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[19] L. Rosenthaler and A. Abelmann, *Pharm. J.* **91**, 144, 186; *Chemical Abstracts* **7**, 3726 (1913).

[20] G. Incze, *Z. anal. Chem.* **56**, 177 (1917); *J. Soc. Chem. Ind.* **36**, 671 (1917).

[21] I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.* **71**, 339 (1927).

[22] N. A. Lazarkevich, *Ukrainskii Khem. Zhur.* **4**, Sci. Pt. 405 (1929); *Chemical Abstracts* **24**, 3456 (1930).

[23] R. L. Vandaveer, *J. Assoc. Official Agri. Chem.* **22**, 563 (1939).

standardizing 0.1*N* HCl with borax, sodium carbonate, and by precipitation as silver chloride. Considerable merit is claimed for borax and carbonate, but the results by silver chloride precipitation are not satisfactory, due, primarily, to the solubility of silver chloride.

Bromocyanogen [24] has been proposed as a universal standard for acids, silver nitrate, and sodium thiosulphate. It is, however, a disagreeable compound to work with, and its use is limited.

The standardization of bases by titration with a previously standardized acid is suitable for control work, but is affected, naturally, by those errors occurring in the initial standardization. It is necessary, therefore, to apply the same procedure to bases as was used for acids, namely, titration by means of a primary standard.

An early attempt to establish a universal standard was the use of ammonium triiodate, $(NH_4)H_2(IO_3)_3$.[25] It was prepared by the action of ammonium chloride on iodic acid, allowing the solution to stand 24–48 hours, and recrystallizing the salt from hot water. It contains no water of crystallization and can be dried over sulphuric acid. Borax [26] may be used for strong bases. Boric acid is very weak and can be titrated only in fairly high concentrations using a reference solution. It does, however, form compounds with polyhydric alco-

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[24] M. Moller, *Z. anal. Chem.* 99, 351 (1934).

[25] E. Riegler, *Bull. assoc. chim. sucr. dist.* 24, 528; *Chemical Abstracts* 1, 705 (1907).

[26] M. G. Mellon and V. N. Morris, *Ind. Eng. Chem.* 17, 145 (1925).

hols, giving strong complex acids which give a sharp end point with phenolphthalein. Glycerine (neutral), glucose, or mannitol may be used. Mannitol is very satisfactory, but when glycerine is used, there is an indicator lag.

The use of potassium chlorate as a standard for alkali has been suggested by van Valkenburg.[27] A solution of the salt (approximately normal) is boiled and reduced, while boiling, with SO_2 according to the equation:

$$3\ SO_2 + KClO_3 + 3H_2O \longrightarrow 3\ H_2SO_4 + KCl$$

The excess SO_2 is boiled off, and the acid titrated with alkali, using phenolphthalein as an indicator.

Potassium binoxalate,[28] and either potassium or sodium acid phthalate[29] are suitable standards, the phthalates, in particular, because of their high equivalent weights.

Ashley and Hulett[30] proposed the use of cadmium sulphate as a standard for alkali. They allowed a solution of the salt to evaporate spontaneously and separated the clear crystals. From a given weight of the clear crystals, a known quantity of sulphuric acid

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[27] H. B. van Valkenburg, *J. Am. Chem. Soc.* 42, 757 (1920).

[28] Yukichi Osaka and Kinji Ando, *J. Tokyo Chem. Soc.* 41, 945 (1920); *Chemical Abstracts* 15, 1472 (1920).

[29] W. S. Hendrixson, *J. Am. Chem. Soc.* 37, 2352 (1915).

[30] S. E. Q. Ashley and G. A. Hulett, *J. Am. Chem. Soc.* 56, 1275 (1934).

was obtained by dissolving the sulphate in water and depositing the cadmium on a mercury cathode. The results agreed with values obtained using benzoic acid, potassium acid phthalate, and constant-boiling hydrochloric acid.

By far the largest class of compounds available for the standardization of bases is the organic acids. Their solubility in water is usually low and they are, for the most part, dissolved and titrated in an alcohol-water mixture.

Phelps and Weed[31] examined a number of organic compounds, namely, succinic acid, succinic anhydride, malonic acid, benzoic acid, phthalic acid, and phthalic anhydride and found excellent agreement. On the other hand, Peters and Sanchelli[32] were unable to duplicate the work of Phelps and Hubbard[33] who had previously used succinic acid for standardizing ammonia. These authors obtained normalities which were high compared with those measured by other methods. Correct results, according to Ljungren,[34] may be obtained with $N/10$ alkalies by dissolving succinic acid in a

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[31] I. K. Phelps and L. H. Weed, *Am. J. Sci.* **26,** 138 (August).

[32] C. A. Peters and V. Sanchelli, *Am. J. Sci.* **41,** 244 (1916).

[33] I. K. Phelps and J. L. Hubbard, *Am. J. Sci.* **23,** 211; *Z. anorg. Chem.* **53,** 361; *Chemical Abstracts* **1,** 1832 (1907).

[34] G. Ljungren, *Svensk Kem. Tid.* **36,** 25 (1923); *Chemical Abstracts* **18,** 1447 (1924).

minimum quantity of CO_2-free water (no more than 10 cc), and using 3–4 drops of 1:1000 phenolphthalein solution as an indicator.

Adipic acid [35, 36] and salicylic acid [37] are satisfactory standards, although the values obtained with the latter [38] are somewhat low. Furoic acid,[39] which possesses the advantage of being soluble in water, gives about the same accuracy as benzoic acid. Aminosulphonic acid [40] and the sulphuric acid salts of aromatic amines [41] have also been used and are capable of reasonable accuracy.

Sulphamic acid, NH_2SO_3H,[42] has been proposed as an alkalimetric standard. It is easily purified, is not hygroscopic, and is soluble in water. Aqueous solutions hydrolyze, on standing, to ammonium acid sulphate.

The standardization of silver nitrate solutions is accomplished either gravimetrically or volumetrically; the

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[35] F. Th. van Voorst, *Chem. Weekblad,* **25,** 22 (1928).

[36] A. H. Meyling, *J. S. African Chem. Inst.* **18,** 23 (1935).

[37] J. Rosicky and J. Tamchyna, *Chem. Listy,* **25,** 468 (1931); *Chemical Abstracts* **26,** 4006 (1932).

[38] S. Skromovsky, *Collection Czechoslov. Chem. Communications* **5,** 143 (1933); *Chemical Abstracts* **27,** 3418 (1933).

[39] H. B. Kellog and Ada M. Kellog, *Ind. Eng. Chem., Anal. Ed.* **6,** 251 (1934).

[40] L. Herboth, *Arch. Phar.* **262,** 517 (1924).

[41] E. Strasser, *Z. anal. Chem.* **82,** 114 (1930).

[42] Sister M. Josetta Butler, G. F. Smith and L. F. Andrieth, *Ind. Eng. Chem., Anal. Ed.* **10,** 690 (1938).

former by precipitation of the silver as silver chloride with a slight excess of sodium chloride to which a small amount of nitric acid has been added, and the latter by titration of known amounts of pure sodium chloride with potassium chromate as an indicator. A blank determination, using the same amount of indicator as in the sample, must be run and the correction subtracted from the sample titration. Ammonium thiocyanate and potassium thiocyanate are generally standardized by direct titration with standard silver nitrate solution, although the recrystallized salt may be used.

The evaluation of potassium ferrocyanide solutions is made with pure zinc oxide. This can be purchased in a high degree of purity and, after a preliminary drying for an hour at 105° C, is ready for use.

On account of its stability and the ease with which it is purified, potassium dichromate still remains an excellent standard substance for sodium thiosulphate solutions. Conflicting statements, however, have appeared in the literature concerning its use in the procedure. Vosburgh[43] states that if the solution is 0.2–0.4 N in HCl, contains 2–3 gm of potassium iodide for every five milliequivalents of dichromate, and is allowed to stand in the dark for 4–10 minutes, the reduction is quantitative. The solution is then diluted to 400 cc with distilled water, and titrated with the thiosulphate solution.

[43] W. C. Vosburgh, *J. Am. Chem. Soc.* 44, 2120 (1922).

On the other hand, Jander and Berte [44] add 15 cc of $N/10$ $K_2Cr_2O_7$ to 40 cc of 2 N KI and 40 cc of concentrated HCl. Complete liberation of iodine takes place in fifteen minutes. If the solution is titrated too quickly, too much thiosulphate is used. Their values, using this procedure, agreed exactly with those obtained by standardization of thiosulphate solution with potassium permanganate and pure iodine.

The reliability of the results, obtained by the use of this standard, has often been questioned. It has been suggested [45] that variations occur due to air oxidation of potassium iodide, and that the reaction is catalyzed by Cr^{+++} ions. Teis [46] found that variable results were obtained when the concentration of potassium iodide, and the time of standing were varied.

Potassium iodate and potassium bromate are satisfactory standards for thiosulphate solutions, but unsatisfactory from the standpoint of their low equivalent weights. Milstead,[47] however, reporting on the standardization of iodine and thiosulphate solutions, states that normalities obtained by use of iodine and unpuri-

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[44] G. Jander and H. Berte, *Z. anorg. allgem. Chem.* **113,** 73 (1924).

[45] K. Bottger and W. Bottger, *Z. anal. Chem.* **69,** 146 (1926).

[46] R. V. Teis, *J. Gen. Chem. (U.S.S.R.)* **1,** 845 (1931); *Chemical Abstracts* **27,** 39 (1933).

[47] K. L. Milstead, *J. Assoc. Official Agri. Chem.* **22,** 567 (1939).

fied analytical grade potassium iodate do not agree, and that some impurity was present which liberated more iodine than a corresponding amount of iodate. The amount of this impurity, which was thought to be sodium iodate, appeared greater after recrystallization.

The use of potassium iodide in the standardization of solutions of low normality has been suggested by Hurka.[48] Briefly, the iodide is oxidized by bromine to iodate, which, in turn, is reacted with sulphuric acid, liberating iodine, which is titrated with the thiosulphate.

Potassium permanganate [49] has been used as a standard for sodium thiosulphate, and accurate results were obtained, providing that the conditions were strictly adhered to. The reaction between $KMnO_4$ and KI takes place in 50–125 cc of 0.7–0.1 N HCl or H_2SO_4. After standing 2–5 minutes, the solution is diluted to 600 cc and titrated.

Potassium biiodate,[50] oxalic acid,[51] and copper [52, 53]

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[48] W. Hurka, *Mikrochemie ver. Microchim. Acta* **28**, 294 (1940).

[49] J. M. Hendel, *Z. anal. Chem.* **63**, 321 (1923).

[50] M. Koenig, *Chimie et industrie,* Special No. 116–7 (Sept. 1925).

[51] N. A. Tananaev and N. A. Lazarkevich, *J. Russ. Phys. Chem. Soc.* **61**, 1909 (1929); *Chemical Abstracts* **24**, 3456 (1930).

[52] T. F. Buerer and C. M. Mason, *Ind. Eng. Chem., Anal. Ed.* **1**, 68 (1929).

[53] S. Popoff, Margaret Jones, C. Rucker and W. W. Becker, *J. Am. Chem. Soc.* **51**, 1299 (1929).

have been suggested as standard substances for thiosulphate solutions. Potassium biiodate can be obtained in a high state of purity, but possesses a low equivalent weight. The titration is carried out in a solution slightly acid with HCl.

If sodium thiosulphate is decomposed by HCl and converted to Na_2CO_3 by ignition with oxalic acid, the Na_2CO_3 may be titrated with standard acid, and the thiosulphate solution evaluated in this manner.

The use of copper * as an analytical standard must depend on the purity of the sample. Copper produced electrolytically is the best source. It is dissolved in sulphuric acid, evaporated to dryness, and taken up in distilled water. The reaction proceeds in a neutral, or nearly neutral, solution in the absence of salts. Potassium iodide is then added to reduce the copper. Acid concentration affects the determination by lessening the amount of iodine liberated, and should not be over 0.2 *N* in sulphuric acid.

Several standard substances are available for the evaluation of iodine solutions. A method commonly used is the titration of the unknown solution with previously standardized sodium thiosulphate. This is necessarily open to errors, which may be additive, arising from the standardization of the thiosulphate solution.

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* See also, Copper Sulphate as a Standard for Thiosulphate Titrations, a review with discussion of the literature, N. Schoorl, *Pharm. Weekblad* 76, 1441 (1939).

Sodium thiosulphate pentahydrate is suitable as a standard substance. According to Kolthoff,[54] its range of stability is great. Below 23% relative humidity it weathers, and above 69% it deliquesces. The anhydrous salt is not recommended, as it is strongly hygroscopic.

Arsenious acid is a very satisfactory standard. It is stable and easily obtainable pure.

Sodium acetomercurithymol sulphonate [55] may be obtained in a high degree of purity. It has a high molecular weight, and reacts with iodine by displacement of the acetomercuric group. It is stated to give more accurate results than arsenious oxide.

Hydrazine reacts with iodine according to the following equation:

$$N_2H_4 + 2\ I_2 \longrightarrow 4\ HI + N_2$$

It is used in the form of hydrazine sulphate, and the reaction takes place in a solution alkaline with sodium bicarbonate. A disadvantage is its low equivalent weight.

Ammonium triiodate,[56] silver nitrate,[57] and potassium

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[54] I. M. Kolthoff and N. H. Furman, *Volumetric Analysis, Vol. II* (1929), p. 360.

[55] C. V. Bordeianu, I. N. Petrescu, L. Staicovici, *Bull. Soc. Stiinte Farm. Romania* **4**, 473 (1939); *Chimie et industrie* **43**, 458.

[56] E. Riegler, *Bull. assoc. chim. sucr. dist.* **24**, 528; *Chemical Abstracts* **1**, 705 (1907).

[57] V. E. Pavloc and S. D. Shein, *J. Russ. Phys. Chem. Soc.* **39**, 943; *Chemical Abstracts* **2**, 772 (1908).

stannous diaquotetrachloride ($K_2SnCl_4 \cdot 2\ H_2O$)[58] have also been proposed as iodometric standards.

The usual method of standardization of potassium permanganate is by means of oxalic acid or sodium oxalate. Hill and Smith[59] recrystallized oxalic acid ($H_2C_2O_4 \cdot 2\ H_2O$), and found that values obtained with permanganate agreed within 0.025% with those obtained using Bureau of Standards sodium oxalate. The vapor pressure of the hydrate at ordinary temperatures is slightly less than that of air at the same temperature. There is, therefore, danger of water condensing as a film on the surface of the crystals. Treadwell and Johner[60] recommend drying the recrystallized and powdered acid in a stream of air which has been passed through a mixture of equal parts of hydrated and hydrous acid. The results, using this procedure, are comparable to those obtained by use of sodium oxalate. Calcium oxalate,[61] prepared from pure calcium oxide, has been used as a standard substance, and satisfactory results are claimed for it.

The use of metallic silver[62] has been proposed, and

[58] T. Karantarsis and L. Capatos, *Compt. rend.* **194,** 1839 (1932).

[59] A. E. Hill and T. M. Smith, *J. Am. Chem. Soc.* **44,** 546 (1922).

[60] W. D. Treadwell and H. Johner, *Helv. Chim. Acta* **7,** 528 (1924).

[61] E. Little and W. H. Beisler, *J. Am. Leather Chem. Assoc.* **14,** 613 (1919).

[62] N. A. Tananaev, *Z. anorg. allgem. Chem.* **136,** 193 (1924).

the standardization of permanganate by it is obtained in the following manner: Ferric alum (0.5–1.0 gm) is dissolved in 100 cc of 7 *N* H_2SO_4 in an Erlenmeyer flask. The solution is saturated with CO_2, and 0.25–0.35 gm silver added. After the silver has dissolved, the solution is cooled rapidly, phosphoric acid added until the solution is colorless, and titrated with permanganate. The reactions involved take place as follows:

(1). $Ag + Fe_2(SO_4)_3 \longrightarrow AgSO_4 + 2\ FeSO_4$

(2). $10FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 \longrightarrow$
$K_2SO_4 + 2\ MnSO_4 + 5\ Fe_2(SO_4)_3 + 8\ H_2O$

The use of iron, Mohr's salt, and arsenious oxide is not entirely satisfactory, since they all possess disadvantages. The purity of iron and Mohr's salt is questionable, and if it is necessary to establish the purity of these compounds by some other means, they lose their significance as standard substances. Ferric ammonium sulphate, which can be obtained pure by recrystallization, may be used as a standard, first reducing all the ferric iron to ferrous iron. Its keeping qualities are not good. The reaction with arsenious oxide does not proceed smoothly. Complex compounds are formed, and the end point is not well defined. Potassium ferrocyanide has been used as a standard substance, but the end point, which is difficult to detect, offsets the advantage of a high equivalent weight. Titration must take

place in dilute solution. DeBeer and Kjort [63] have used ferrocyanide for the standardization of dilute solutions, with erioglaucine as an indicator.

Evidence has been presented [64] to show that results of standardization of permanganate with sodium oxalate are not reliable to less than 1 part in 1000. Fused potassium iodide, titrated by Andrew's method to ICl, shows agreement within 0.03%, and may be regarded as a more reliable standard.

Further work [65] with potassium iodide for standardization of strong oxidizing agents such as permanganate and ceric sulphate involves the use of acetone. The iodide is dissolved in water acid with H_2SO_4, and pure acetone added. The solution is titrated with the oxidizing agent, using three drops of 0.025 *N* ferrous phenanthroline sulphate as an indicator. The end point is reached when the solution remains colorless for thirty seconds. The results are generally low, due to a reaction between acetone and the oxidizing agent.

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[63] E. J. deBeer and A. M. Hjort, *Ind. Eng. Chem., Anal. Ed.* 7, 120 (1935).

[64] I. M. Kolthoff, H. A. Laitinen and J. J. Lingane, *J. Am. Chem. Soc.* **59**, 429 (1937).

[65] I. M. Kolthoff and H. A. Laitinen, *J. Am. Chem. Soc.* 61, 1690 (1939).

CHAPTER V

Standard Solutions of Acids and Bases

Standardization of Hydrochloric Acid

Molecular Weight: 36.465 HCl
Equivalent Weight: 36.465
Grams of Constant Boiling Acid/Liter for

1	Normal Acid	180.193 gm
0.5	" "	90.097 gm
0.1	" "	18.019 gm

Preparation of Constant Boiling Acid

Since ordinary concentrated hydrochloric acid [1] varies slightly in strength, it wold seem useful to have some definite standard solution which would not vary in percentage composition. Hulett and Bonner [2] recommended the use of constant-boiling acid for standard solutions. Foulk and Hollingsworth [3] made an extremely accurate investigation. They recommend start-

[1] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **17**, 756 (1925).

[2] G. A. Hulett and W. D. Bonner, *J. Am. Chem. Soc.* **31**, 390 (1909).

[3] C. W. Foulk and M. Hollingsworth, *J. Am. Chem. Soc.* **45**, 1220 (1923).

ing with hydrochloric acid solution of specific gravity 1.18. Aftr three-quarters of the mixture have been distilled, the receivers are changed and the distillation continued until only a few cubic centimeters are left in the still. This last distillate is considered to be constant-boiling acid. The speed of distillation has very little influence on the acid content. If, however, the original acid is diluted to a specific gravity of 1.0959 at 25° C, three-quarters of the distillate may be used. Discard the first quarter and continue distillation until only 50–60 cc are left. In this way, it is easy to obtain a definite standard solution within an accuracy of 0.05 per cent.[4] Barometric pressure must be recorded, as the percentage composition varies. The following table (after Foulk and Hollingsworth)[3] gives the composition of constant-boiling acid at various pressures.

Pressure during Distillation mm of Mercury	% HCl Referred to Vacuum	Wt. of Distillate Containing 1 Mol of HCl when Weighed on Air
780	20.173	180.621
770	20.197	180.407
760	20.221	180.193
750	20.245	179.979
740	20.269	179.766
730	20.293	179.551

Store the constant-boiling acid in glass-stoppered bottles. From the barometric pressure, calculate the percentage composition and label the bottles accordingly.

[4] Kolthoff and Furman, *Volumetric Analysis Vol. II,* 74 (1929).

Standardization of Normal and Half Normal Acid with Sodium Carbonate

If the distillation of constant-boiling acid has been carried out at 760 mm, weigh out accurately 180.193 gm and 90.097 gm respectively for normal and half normal acid and make up to 1 liter with distilled water; otherwise weigh accurately equivalent amounts depending on the barometric pressure at the time of distillation.

According to Lunge, sodium bicarbonate is quantitatively converted into the carbonate by heating to 270–300° C. The procedure is as follows: Place 10 gm of the bicarbonate [5] in a silver crucible, and place in a shallow sand bath, imbedding the crucible so that the level of the sand is slightly above the level of bicarbonate in the crucible. Suspend a thermometer in the crucible in such a way that it acts as a stirring rod. Heat the sand bath so that the temperature rises at the rate of 5° C a minute, stirring the bicarbonate continually. This stirring is important, especially when relatively large amounts are to be converted to carbonate. After heating between 270 and 300° C for at least half an hour, the crucible is transferred to a desiccator and cooled. A recent paper by Smith and Croad [6]

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[5] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 18, 759 (1926).

[6] G. F. Smith and G. F. Croad, *J. Ind. Eng. Chem., Anal. Ed.* 9, 141 (1937).

has shown that an appreciable error results when the temperature is allowed to exceed 300° C. The carbonate is transferred to a bottle having a tight-fitting, ground glass stopper. When weighing, the bottle should be opened only for brief intervals, and the weighing accomplished as quickly as possible, because of the fact that carbonate changes to the monohydrate rapidly.

If, for any reason, it is inconvenient to prepare carbonate from the bicarbonate, it is possible to use an analytical grade sodium carbonate, after washing with alcohol and drying at 100° C, since the chief impurity is sodium hydroxide, which is soluble in alcohol.

Procedure for Standardization

Weigh out sufficient sodium carbonate to give a titration of around 40 cc. In the case of normal acid, use 2.12 gm, and 1.06 gm for half normal acid. Dissolve the carbonate in the smallest possible quantity of water. Titrate, using methyl yellow as an indicator, to the first change. Just before the end point is reached, the solution should be stirred or shaken vigorously to remove carbon dioxide.

Reactions: $Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$

Calculations: Equivalent weight of $Na_2CO_3 = 53.0$

$$\text{Normality} = \frac{\text{Weight of } Na_2CO_3}{0.053 \times \text{Titration in cc}}$$

Standardization of Tenth Normal Acid by Preciptation as Silver Chloride

Tenth normal acid is prepared by accurately pipetting 100 cc of normal acid into a volumetric flask and diluting to one liter. It is standardized as follows: Pipette 50 cc portions into 250 cc beakers. Add an excess of silver nitrate solution to precipitate the acid as silver chloride. Bring to a boil to coagulate the precipitate. Let stand in the dark until cool, and filter through previously dried and weighed Gooch crucibles.

Reaction: $HCl + AgNO_3 \longrightarrow AgCl + HNO_3$

Mol wt. $AgCl = 143.34$ 1 cc $HCl \approx 0.14334$

$$\text{Calculations: Normality} = \frac{\text{Wt. of silver chloride}}{50 \times 0.14334}$$

Alternative Method of Standardization Using Borax

Borax [7] has long been recognized as a primary standard for acids. The greatest obstacle, however, has been the difficulty in preparing the anhydrous salt and preserving it in the anhydrous state. In an article,[8, 10] it is stated that borax, recrystallized as the decahydrate from water and kept over a solution of sodium bromide having a relative humidity of 60%, is extremely stable over a long period. Added to this is the advantage that borax does not lose water of crystallization during the time of weighing.

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[7] Kolthoff and Furman, *Volumetric Analysis Vol. II*, 93 (1929).

Pure borax may be prepared as follows [8]: 45 gm of borax are added to 150 cc of water at room temperature, stirred well, and allowed to stand for several hours. The borax is filtered off through a Büchner funnel, washed twice with water, then with two portions of 95% ethyl alcohol, and finally twice with ethyl ether, each washing being followed by suction to remove the wash liquid. Use 5 cc of alcohol and ether for every 10 gm of borax. Transfer the crystals to a watch glass, and allow them to stand at room temperature a short time to permit evaporation of the ether, then transfer them to a desiccator containing a saturated sodium chloride solution as a desiccant. It was found that sodium chloride could be substituted for sodium bromide, since the relative humidity of the saturated solution [9] is 60%. To insure the crystals reaching equilibrium, they should be left in the desiccator for a week before using.

Standardization of Normal, Half Normal, and Tenth Normal Acid

Prepare the normal solutions in accordance with the instructions given in the preceding methods.

Borax, $Na_2B_4O_7 \cdot 10\, H_2O$, has a molecular weight of 381.43, and an equivalent weight of 190.76, which

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[8] F. H. Hurley, *J. Ind. Eng. Chem., Anal. Ed.* 8, 220 (1936).

[9] Kolthoff and Sandell, *Inorg. Quant. Analysis* (1929). 123.

means that large samples can be used for standardization, thus reducing the error in weighing.

The procedure is as follows: Weigh out 6.00 gm, 3.00 gm, and 0.65 gm respectively for normal, half normal, and tenth normal acid. Dissolve in the smallest quantity of distilled water. Add several drops of methyl red and titrate to the first visible change.

Reaction: $Na_2B_4O_7 + 2\,HCl + 5\,H_2O \longrightarrow 4\,H_3BO_3 + 2\,NaCl$

Calculations: $\text{Normality} = \dfrac{\text{Wt. of Borax}}{0.19076 \times \text{Titration in cc}}$

Note: In the standardization of tenth normal acid, it is necessary to boil the water first to remove carbon dioxide, since failure to do so introduces a real error in the standardization. In the case of normal and half normal acid, this precaution is not necessary.

Standardization of Normal, Half Normal, and Tenth Normal Acid with Thallous Carbonate

Thallous carbonate, with its high equivalent weight (468.79), is an excellent primary standard for acids and has also been used for the standardization of iodate solutions.

The following procedure for the standardization of acids is based on the method recommended by Berry.[11]

A suitable quantity of the salt (or a corresponding volume of solution) is dissolved in distilled water and

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[10] F. H. Hurley, *J. Ind. Eng. Chem., Anal. Ed.* 9, 237 (1937).

[11] A. J. Berry, *Analyst,* 64, 27 (1939).

titrated, using methyl orange as an indicator.* The *p*H at the end point is 3.8.

Reaction: $Tl_2CO_3 + 2\,HCl \longrightarrow 2\,TlCl + H_2O + CO_2\uparrow$

Calculations: $\text{Normality} = \dfrac{\text{Wt. } Tl_2CO_3}{0.46879 \times \text{cc Titration}}$

Standardization of Sulphuric Acid

Molecular Weight: 98.08 H_2SO_4
Equivalent Weight: 49.04

Preparation of the Solution

Weigh accurately the amount of acid [12] necessary to give the required normality, taking into consideration the strength of the acid as recorded on the original container. Add cautiously to a relatively large amount of water, and when cool, transfer to a volumetric flask and make up to volume.

Standardization with Barium Chloride

Pipette 25 cc of the volumetric solution into a 400 cc beaker, add 250 cc of distilled water and 3 cc of concentrated hydrochloric acid. Heat to boiling and precipitate at the boil with 10% barium chloride. Allow

*Hickman and Linstead [*J. Chem. Soc.* **121**, 2502 (1922)] recommend screening the methyl orange indicator with xylene cyanine FF.

[12] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem., Anal. Ed.* **17**, 756 (1925).

the barium chloride [12] to run in drop by drop, stirring vigorously meanwhile. Popoff [13] has shown that the temperature at which the barium sulphate is precipitated influences greatly the size of the crystals. Cover the beaker with a watch glass and let the precipitate stand over night on the steam plate. Filter, hot, through a quantitative filter paper, and wash the precipitate at least ten times with hot water, or until the filtrate gives no precipitate with silver nitrate. Ash carefully in a platinum crucible, or a clean porcelain crucible, to constant weight.

Reaction: $H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2HCl$

Calculations: Factor $\dfrac{H_2SO_4}{BaSO_4} = \dfrac{98.08}{233.42} = 0.4202$

$$0.4202 \times \frac{1000}{25} \times \text{wt. of ppt.} = \text{wt. of } H_2SO_4 \text{ in gm/l}$$

$$\text{Normality} = \frac{49.04}{\text{wt. of } H_2SO_4}$$

The standardization of sulphuric acid is accomplished most accurately by precipitation as barium sulphate. However, the methods involving the use of borax or carbonate, as described under hydrochloric acid, give equally accurate results.

Note: Picric acid (10 cc of a saturated solution) may be added to the sample of sulphuric acid to be standardized, before precipitation as barium sulphate. The solution is brought to boiling and the

[13] S. Popoff and E. W. Neuman, *Ind. Eng. Chem., Anal. Ed.* 2, 45 (1930).

usual procedure for precipitation followed. If the solution is boiled gently for 5–10 minutes, and then allowed to stand on a steam plate for an hour, the precipitate may be filtered, ignited, and weighed. The results obtained may not be strictly accurate, since, if the filtrate from this proecdure is allowed to stand over night, it is possible to obtain a slight amount of precipitate, representing barium sulphate, which, at the time of filtration, was in the colloidal state. It is also important that the acidity, after precipitation, should not be too high, since hydrochloric acid exerts a solvent effect, or possibly a peptizing action on freshly precipitated barium sulphate. Picric acid may contain soluble sulphate as an impurity. If there is any doubt as to the purity, it is necessary to run a blank determination on the amount of picric acid ordinarily used in the determination.

Standardization of Sodium Hydroxide

Molecular Weight: 40.00 $NaOH$
Equivalent Weight: 40.00

Preparation of the Solution

Standard solutions of sodium hydroxide[14] should be prepared from a concentrated stock solution.[15,16] This is a 50% solution, so called Sörenson's "oily alkali," and is made by dissolving one pound of pellet caustic in 450 cc of distilled water. The solution will be cloudy, due to carbonate[17] which is always present. Let the solution stand for several days or until the carbonate has settled out and the liquid is clear, before using. If

[14] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

[15] Hillebrand and Lunden, *Applied Inorganic Analysis* (1929), 139.

[16] Kolthoff and Furman, *Volumetric Analysis Vol. II* (1929), 77.

[17] J. E. S. Han and T. Y. Chao, *J. Ind. Eng. Chem.. Anal. Ed.* 4, 229 (1932).

it is necessary to use immediately, the solution may be centrifuged.[18] The solution is best kept in a Pyrex Erlenmeyer, tightly closed with a rubber stopper.

Standardization with Hydrochloric Acid

Weigh out the equivalent of alkali by withdrawing the stock solution by means of a pipette, and transferring to a weighing bottle. If tenth normal alkali, or less, is to be prepared, make up to volume with water which has been previously boiled to expel carbon dioxide. Pipette 25 cc of previously standardized hydrochloric acid into an Erlenmeyer flask and titrate to an end point, using phenolphthalein as an indicator. The accuracy of this standardization will depend upon the accuracy with which the normality of the hydrochloric acid was determined.

Reaction: $NaOH + HCl \longrightarrow NaCl + H_2O$

Calculations: $N_{NaOH} \times V_{NaOH} = N_{HCl} \times V_{HCl}$

where N = normality and V = volume of solution used

Standardization with Potassium Acid Phthalate [19, 20]

Potassium acid phthalate may be obtained pure from the Bureau of Standards, or the pure salt may be re-

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[18] N. Allen and G. W. Low, *J. Ind. Eng. Chem., Anal. Ed.* 5, 192 (1933).

[19] F. E. Dodge, *J. Ind. Eng. Chem.*, 7, 29 (1915).

[20] W. S. Hendrixson, *J. Am. Chem. Soc.* 37, 2353 (1915); 42, 724 (1920).

crystallized from water and dried at 105° C. Weigh a sufficient quantity of the salt to give a titration of about 40 cc. Dissolve in a small quantity of distilled water and titrate with alkali to an end point with phenolphthalein.

Reaction: $$NaOH + \begin{matrix} HOOC \\ KOOC \end{matrix} \Big\rangle C_6H_4 \longrightarrow C_6H_4 \Big\langle \begin{matrix} COONa \\ COOK \end{matrix} + H_2O$$

Calculations: The equivalent weight of potassium acid phthalate is 204.06

$$\text{Normality} = \frac{\text{Wt. of } KHO_4C_8H_4}{0.20406 \times \text{cc of alkali}}$$

Standardization with Potassium Bi-iodate

The salt may be obtained pure. If necessary, it can be recrystallized from water and dried at 105° C. It has the advantage of a high equivalent weight, and is not hygroscopic. Dissolve enough of the salt to give a titration of about 40 cc in a small quantity of distilled water and titrate using phenolphthalein as an indicator.

Reaction: $$NaOH + KH(IO_3)_2 \longrightarrow NaIO_3 + KIO_3 + H_2O$$

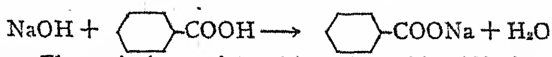
Calculations: The equivalent weight of potassium bi-iodate is 389.85

$$\text{Normality} = \frac{\text{Wt. of } KH(IO_3)_2}{0.3899 \times \text{cc of alkali}}$$

Standardization with Benzoic Acid

Pure benzoic acid may be purchased from the Bureau of Standards. It is, however, readily obtainable from other sources in a high degree of purity. Alcohol, which has been carefully neutralized to the phenolphthalein end point with alkali, is used as a solvent.

A weighed quantity of benzoic acid, sufficient to give a titration of around 40 cc, is dissolved in 25 cc of the neutralized alcohol and titrated to an end point

Reaction: 

Calculations: The equivalent weight of benzoic acid is 122.46

$$\text{Normality} = \frac{\text{Wt. of benzoic acid}}{0.1225 \times \text{cc of alkali}}$$

Standard solutions of alkali should be stored in bottles made of alkali-resistant glass. Ordinary glass bottles are appreciably attacked on standing. As a precaution against contamination of the standard alkali from carbon dioxide in the air, it is well to equip the containers with a soda-lime tube.

Standardization of Potassium Hydroxide

Molecular Weight: 56.10 — KOH
Equivalent Weight: 56.10

Preparation of the Solution

Potassium hydroxide,[21] unfortunately, cannot be prepared carbonate-free as easily as sodium hydroxide, since potassium carbonate is appreciably soluble in the concentrated alkali. Kolthoff[22, 23] suggests the follow-

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[21] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

[22] I. M. Kolthoff, *Z. Anal. Chem.* 61, 48 (1922).

[23] Kolthoff and Furman, *Volumetric Analysis Vol. II* (1929), 77.

ing method: Prepare a 1.1 N solution of potassium hydroxide. Add 50–80 cc of milk of lime and shake for one hour. Allow to settle for several days and siphon off the clear liquid. The solution must be protected from the carbon dioxide of the air by means of a soda lime tube. After determining the normality of this stock solution, it may be diluted to the desired strength. If the directions are properly carried out, the solution will contain no more than 1–2 mg of calcium per liter. The presence of carbonate may be determined qualitatively by adding some of the alkali to a test tube containing $N/2$ barium nitrate or chloride, closing the tube quickly after addition, and shaking. No turbidity should form after ten minutes standing.

Carbonate-free potassium hydroxide may also be prepared by dissolving the alkali in a small quantity of alcohol. After the carbonate settles out, the clear solution is decanted into a volumetric flask containing previously boiled distilled water, and made up to volume.

Standardization of potassium hydroxide is carried out in the same way as for sodium hydroxide (q.v.).

Standardization of Barium Hydroxide and Ammonia

Molecular Weight:	171.38	$Ba(OH)_2$
Equivalent Weight:	85.69	
Molecular Weight:	35.05	NH_4OH
Equivalent Weight:	35.05	

Standard solutions of these alkalis are comparatively little used, and are, moreover, extremely hard to keep. The titer will vary from day to day, necessitating re-standardization each time the solution is used.

Preparation and Standardization of Barium Hydroxide

Barium hydroxide, which has been treated with barium chloride to reduce the solubility of barium carbonate, is best used for the standard solution. It must be kept carefully protected from the carbon dioxide of the air, and must be made up with previously boiled distilled water. It is most easily standardized against standard acid, using phenolphthalein as an indicator. (See directions for standardizing sodium hydroxide with hydrochloric acid.)

Preparation and Standardization of Ammonia

Ammonia,[24] due to its volatility at ordinary temperatures, is very unsatisfactory as a standard reagent. Weigh, in a closed vessel, the approximate amount of ammonia and transfer quickly to a volumetric flask containing boiled distilled water. Stopper and mix, make up to volume, transfer to tightly stoppered container, and keep in a cool place. Standardize against hydrochloric acid, using methyl orange as an indicator. Methyl red may be preferred, since the transition range is sharper.

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[24] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **17**, 756 (1925).

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Benzoic Acid as an Acidimetric Standard, G. W. Morey, *J. Am. Chem. Soc.* **34,** 1027 (1912).

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CHAPTER VI

Standard Solutions of Precipitation Reagents

Standardization of Potassium or Ammonium Thiocyanate

Molecular Weight:	97.17	KSCN
Equivalent Weight:	97.17	
Molecular Weight:	76.11	NH_4SCN
Equivalent Weight:	76.11	

Preparation of Potassium or Ammonium Thiocyanate

The thiocyanates are hygroscopic, and therefore, the theoretical amounts of the salts cannot be weighed with any accuracy. It is necessary to weigh out slightly more than the theoretical. Approximate amounts are weighed out, and made up to one liter. Of the two, ammonium thiocyanate [1] is better adapted for standard solutions.

Recent work by Kolthoff and Lingane [2] has shown that potassium thiocyanate,[1] when recrystallized and properly dried, is suitable for a primary standard.

[1] Recommended Specifications for Analytical Reagent Chemicals. *Ind. Eng. Chem.* 17, 756 (1925).

[2] I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.* 57, 2126 (1935).

Below a relative humidity of 45%, the dried material keeps well, but should be protected from light.

To prepare potassium thiocyanate for a standard solution, the reagent-grade salt may be dried at 150° C for three hours. If excessive moisture causes caking during the first hour of drying, the sample should be removed, the cake broken up by grinding and returned to oven for the remainder of the drying period.

Procedure

Pipette 25 cc of a standard solution of silver nitrate[3] into a 400 cc beaker, and add about 100 cc of distilled water. Now add 5 cc of a saturated solution of ferric ammonium alum[3] acidified with nitric acid, and titrate with the volumetric solution of thiocyanate to the first permanent appearance of a red brown coloration. Samples of silver nitrate of known purity may be titrated in the same manner.

Reaction: $KSCN + AgNO_3 \longrightarrow AgSCN + KNO_3$

$NH_4SCN + AgNO_3 \longrightarrow AgSCN + NH_4NO_3$

Calculations: Standardization with standard silver nitrate

$$N_{SCN} = \frac{N_{AgNO_3} \times V_{AgNO_3}}{V_{SCN}}$$

Standardization with solid silver nitrate.
Equiv. Wt. 169.89

$$\text{Normality} = \frac{\text{Wt. of } AgNO_3}{0.16989 \times \text{Titration in cc}}$$

[3] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 18, 759 (1926).

Note: If ferric ammonium alum produces a cloudy soltion in water, the addition of a few drops of nitric acid clears the solution. Ferric nitrate may be used in place of ferric alum.

The red brown color observed at the end point of the titration is due to the formation of ferric thiocyanate.

Standardization of Silver Nitrate

Molecular Weight: 169.89 $AgNO_3$
Equivalent Weight: 169.89

Preparation of the Solution

Reagent-grade silver nitrate[4] may be used. This approaches 100% so closely that only a little more than the theoretical amount need be weighed out. The solution should be made up and transferred to a brown bottle as soon as possible. It is essential that the solution be kept free from dust and organic matter, in order to avoid any reduction. With this care, the solution should keep indefinitely.

Standardization with Sodium Chloride

Weigh[5] 0.20–0.25 gm of precipated sodium chloride and dissolve in 20 cc of distilled water in a casserole or evaporating dish. Add 1.5 cc of a 5% solution of potassium chromate[6] and titrate to the first permanent tinge of red. Titrate slowly with constant stirring.

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[4] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

[5] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 20, 979 (1928).

[6] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem., Anal. Ed.* 1, 171 (1929).

Reaction: $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$

$KCrO_4 + AgNO_3 \longrightarrow AgCrO_4 + KNO_3$ (Indicator)

Calculations: The equivalent weight of sodium chloride is 58.45

$$\text{Normality} = \frac{\text{Wt. of NaCl}}{0.05845 \times \text{cc } AgNO_3}$$

Standardization with Ammonium Thiocyanate

Silver nitrate may be standardized against a previously standardized solution of ammonium thiocyanate.

Pipette 25 cc of silver nitrate into a 400 cc beaker containing 200 cc of distilled water and 5 cc of saturated ferric ammonium alum. The solution is titrated with thiocyanate to the first appearance of a permanent red brown color.

Reaction: $AgNO_3 + NH_4SCN \longrightarrow AgSCN + NH_4NO_3$

$Fe_2(SO_4)_3(NH_4)_2SO_4 + 6NH_4SCN \longrightarrow 2Fe(SCN)_3 + 4(NH_4)_2SO_4$ (Indicator)

Calculations: $N_{AgNO_3} \times V_{AgNO_3} = N_{NH_4SCN} \times V_{NH_4SCN}$

Kolthoff and Lingane[7] state that potassium thiocyanate, recrystallized from water and dried for a short time at 200° C, can be used for standardizing silver nitrate solution.

Note: Pure sodium chloride may be prepared by passing hydrochloric acid gas, made by allowing concentrated sulphuric acid to drop slowly on solid sodium chloride, into a concentrated salt solution. The pure salt will precipitate. It is filtered on a Büchner funnel and washed with several small portions of distilled water. Dry at 105° C and store in a glass-stoppered bottle. Always dry the sodium chloride for an hour at 105° C before using to standardize silver nitrate solutions.

[7] I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.* **57**, 2126 (1935).

Standardization of Potassium Ferrocyanide

Molecular Weight: 422.33 $K_4Fe(CN)_6 \cdot 3H_2O$
Equivalent Weight: 211.17

Preparation of the Solution

Weigh out the required amount of the salt and make up to volume. The solution, on standing, oxidizes slightly, forming some ferricyanide. As diphenylamine[8] and diphenyl benzidine are sometimes used as internal indicators in preference to the outside indicator uranyl nitrate, and are aided by the presence of ferricyanide, the solution is allowed to age for several weeks before standardizing, or a maximum of 150 milligrams of potassium ferricyanide per liter is added, whereupon the solution may be standardized immediately. If either diphenylamine or diphenyl benzidine is used, a 1% solution in concentrated H_2SO_4 is made up, and 0.2 cc used per 100 cc of solution. In using diphenylamine, a titration correction must be applied. Diphenyl benzidine, however, is independent of this correction. The color change is to a deep blue color in both cases. Temperature also affects the sensitivity of these indicators. If uranyl nitrate is used, a 1% solution in water is recommended.

Standardization

Weigh out appropriate samples of pure zinc oxide

[8] W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* 49, 356 (1927).

calculated to give titrations of around 40 cc. Dissolve in dilute H_2SO_4 and dilute to 100 cc. Add $(NH_4)_2SO_4$, heat to 60° C and titrate immediately. Do not let the temperature drop below 50° C. If it does, reheat the solution and continue the titration. If an internal indicator is used, the color change is from a light bluish green to a deep blue. In dilute solutions, this change is not evident. In the case of uranyl nitrate, the indicator is spotted on a white porcelain plate. When the end point is approached, the solution should be spotted for every 0.10 cc of ferrocyanide added. A dark brown ring or coloration developing within 2–3 seconds is taken as the end point.

Reaction

$$2K_4Fe(CN)_6 + 3ZnSO_4 \longrightarrow K_2Zn_3[Fe(CN)_6]_2 + 3K_2SO_4$$

The titration is carried out in hot solution because at room temperature, although the above reaction goes to completion, the freshly formed zinc complex reacts with the uranyl nitrate indicator. It is gradually converted to an allotropic form which does not react with the indicator. Heating the solution converts it immediately to this latter phase.

Calculations

Since ferrocyanide is used, for the most part, in the determination of zinc, it is usually evaluated in terms of zinc oxide. In other words, $\frac{\text{Wt. of ZnO}}{\text{Titration in cc}}$ will represent the titer of the solution. A customary figure of 21.6 gm of potassium ferrocyanide gives approximately 1 cc $\approx$ 0.006 gm zinc oxide.

Supplementary References

Standardization of Siver Nitrate Solutions Used in Chemical Studies of Sea Water, T. G. Thompson, *J. Am. Chem. Soc.* **50,** 681 (1928).

Bartholow Park, *J. Am. Chem. Soc.* **54,** 180 (1932).

CHAPTER VII

Standard Solutions of Oxidizing Reagents

Standardization of Iodine

Atomic Weight:	126.92	I_2
Equivalent Weight:	126.92	

Preparation of the Solution

Since there is always a possibility of iodine[1] containing chlorine, bromine, or water as impurities, it is usually advisable to resublime it. This may be done very simply, using the apparatus shown in Figure 1. The iodine crystals are heated slowly with a very small flame, and the iodine sublimes in crystals on the cooled portion of the water-cooled, round-bottom flask. The sublimed iodine is transferred to a glass-stoppered bottle.

In making standard solutions of iodine, it is necessary to dissolve the iodine in a solution of potassium

[1] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

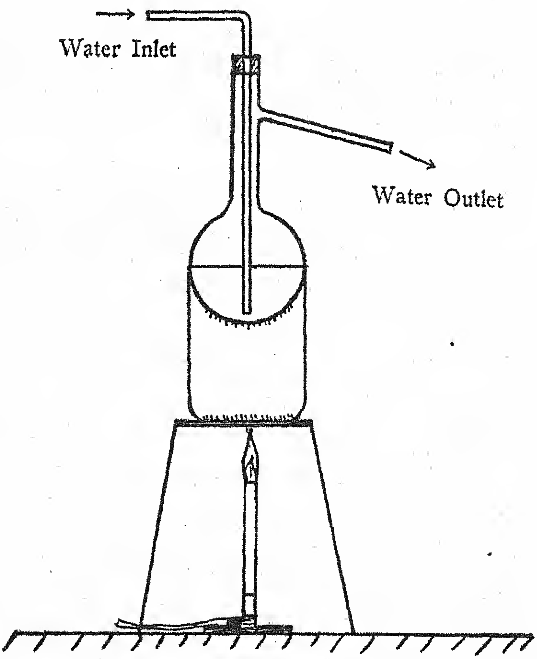

FIG. I

iodide.[2] Therefore, the following procedure is used in making a 0.1 *N* solution. Weigh accurately 12.692 gm of sublimed iodine into a glass-stoppered tall-form weighing tube. Dissolve 25 gm of potassium iodide in 35–40 cc of water. Uncover the weighing bottle and add about 20 cc of this solution. Swirl gently to dissolve the bulk of the iodine and transfer to a liter

[2] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 19, 645 (1927).

volumetric flask. Rinse the weighing tube with the remainder of the iodide solution, quantitatively transferring all of the iodine to the liter flask. Add no water until all the iodine has dissolved. After diluting to volume, transfer to a brown bottle. Iodine solutions are not stable to light, decomposition taking place with the formation of hydriodic acid. A high room temperature also affects them to the point of volatilizing some iodine. Hence, it is necessary to standardize the solutions frequently.

Standardization against 0.1 N Thiosulphate

Aliquots of previously standardized thiosulphate solution are transferred to Erlenmeyer flasks and diluted to 150 cc. The solution is titrated with the iodine to be standardized to a permanent blue end point, using freshly prepared starch as an indicator.

Reaction: $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

Calculations: $N_{I_2} \times V_{I_2} = N_{Na_2S_2O_3} \times V_{Na_2S_2O_3}$

Standardization with Arsenious Oxide

Weigh accurately 0.2000 gm of arsenious oxide,[3] which will give a titration of 40 cc, and dissolve in 10 cc of *N* sodium hydroxide. Dilute to 150 cc and add HCl until the solution is faintly acid. Add, cautiously, enough of a concentrated solution of sodium bicarbonate to represent 2–3 gm of the salt. Add starch and titrate to a permanent blue end point. Cover the

[3] Obtainable from the U. S. Bureau of Standards.

beakers with a watch glass while adding the bicarbonate:

Reactions: $As_2O_3 + 6NaOH \longrightarrow 2Na_3AsO_3 + 3H_2O$
$Na_3AsO_3 + 3HCl \longrightarrow H_3AsO_3 + 3NaCl$
$H_3AsO_3 + 3NaHCO_3 \longrightarrow Na_3AsO_3 + 3H_2O + 3CO_2$
$Na_3AsO_3 + I_2 + 2NaHCO_3 \longrightarrow Na_3AsO_4 + 2NaI + H_2O + 2CO_2\uparrow$

The arsenious oxide dissolves more readily in sodium hydroxide than in bicarbonate. The titration, however, must be carried out in a solution alkaline with bicarbonate. It is for this reason that the solution containing an excess of caustic is neutralized with acid.

Calculations: The equivalent weight of arsenious oxide is 49.46

$$\text{Normality} = \frac{\text{Wt. of } As_2O_3}{0.04946 \times \text{cc Titration}}$$

Recrystallized sodium thiosulphate may be used as a primary standard. It should be kept in a container at a definite humidity, such that only the pentahydrate can exist. A stock solution of arsenious oxide may be prepared by accurately weighing 4.946 gm, dissolving in 40 cc of 1 *N* NaOH, acidifying with HCl until neutral to litmus, and making up to one liter. Kolthoff [4] states that a solution made according to these directions is stable over a long period.

Note: The importance of potassium iodide should not be underestimated. It is essential that potassium iodide be present, particu-

[4] Kolthoff and Furman, *Volumetric Analysis, Vol. I* (1929), 235.

larly in cases where the iodine titration is small; one cc of 10% solution is sufficient for a volume of 200–300 cc. Omission causes consumption of iodine. Potassium iodide is, of course, supplied by the standard solution, but if the probable titration is unknown, it is safer to add more.

The reason for adding the iodide to the standard solution is that it increases the solubility, and decreases the vapor pressure of the iodine, thus reducing the possibility of loss by volatilization.

Standardization of Sodium Thiosulphate

Molecular Weight: 248.19 $Na_2S_2O_3 \cdot 5H_2O$
Equivalent Weight: 248.19

Preparation of the Solution

For a 0.1 *N* solution, 24.82 gm are weighed out, dissolved, and made up to one liter. The anhydrous salt should never be used for volumetric solutions because of the uncertainty in its composition. The hydrated salt [5] is obtainable in a high degree of purity in the market and may be used without further purification. It has been stated that a 0.1 *N* solution can be made by simply weighing accurately the required amount of the salt and diluting to exact volume, but this is not safe practice, since discarding the effect of manual errors and errors due to uncalibrated apparatus, thiosulphate in commercial lots sometimes shows evidence of the presence of the lower hydrates, which are noticeable as a powdery deposit on the surface of the crystals.

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[5] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 18, 759 (1926).

Standardization with Iodine

A previously standardized solution of iodine may be used. An aliquot is titrated with the thiosulphate. Add starch near the end point and titrate to the disappearance of the blue color. Iodine itself may be used as a primary standard. Sublime the iodine acccording to the directions given under the *Standardization of Iodine*. Weigh accurately a small weighing tube with a ground glass stopper containing 2–3 gm of potassium iodide in 2–3 cc of water. The heat of solution of potassium iodide is negative, and it is necessary to wait until the weighing tube and solution have attained room temperature before weighing. Now add quickly about 0.5 gm of sublimed iodine and weigh again. The difference is the exact amount of iodine added. The stoppered weighing tube is transferred to a 300 cc Erlenmeyer flask containing 150 cc of distilled water and allowed to open *only under the water*. The solution is now titrated in the usual manner.

Reaction: $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

Calculations: $N_I \times V_I = N_{Na_2S_2O_3} \times V_{Na_2S_2O_3}$

Iodine has an equivalent weight of 126.92

Calculations: $\text{Normality} = \dfrac{\text{Wt. of Iodine}}{0.12692 \times \text{cc Titration}}$

Standardization with Potassium Iodate

Potassium iodate may be purchased in a high state of purity, or the commercial salt may be recrystallized

from water and dried at 180° C. Its great disadvantage is its low equivalent weight: 35.67.

Weigh out 0.15 gm of the salt and dissolve in 50 cc of distilled water. Add 20 cc of a 15% potassium iodide solution. Make the volume up to 150 cc and add 5 cc of concentrated HCl. Titrate immediately. Add starch near the end point and titrate to the disappearance of the blue color.

Note: In all titrations where iodine is liberated, it is best to carry out operations in an Erlenmeyer flask, or stoppered flask, to minimize loss of iodine.

Reaction: $KIO_3 + 5KI + 6HCl \longrightarrow 6KCl + 3I_2 + 3H_2O$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

Calculations: $\text{Normality} = \dfrac{\text{Wt. of } KIO_3}{0.03567 \times \text{cc Titration}}$

Standardization with Potassium Bromate

The same disadvantage exists with this salt as with the iodate, namely, its low equivalent weight, which is 27.84. It also has the disadvantage of sometimes containing bromide. This may be tested for, qualitatively, by adding 1–2 cc of 4 N H_2SO_4 to a 1% solution. After five minutes, no color should develop. The bromate-iodide-acid reaction does not take place as quickly as the iodate-iodide-acid. After addition of acid, it is necessary to let the mixture stand for several minutes before proceeding with the titration. Also, the concentration of the acid is an important factor. The following procedure is satisfactory: Weigh 0.12 gm of potas-

sium bromate into an Erlenmeyer flask, and dissolve in 50 cc of distilled water. Add 20 cc of 15% potassium iodide solution and dilute to 150 cc. Now add 15 cc of 10% H_2SO_4, stopper the flask, and let stand for three minutes. Titrate, using starch as an indicator.

Reaction: $KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3Br_2 + 3H_2O$

$Br_2 + 2KI \longrightarrow 2KBr + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

Calculations: The equivalent weight of $KBrO_3$ is 27.84

$$\text{Normality} = \frac{\text{Wt. of } KBrO_3}{0.02784 \times \text{Titration in cc}}$$

Standardization with Potassium Dichromate[6, 7, 8]

Potassium dichromate[9] is another salt which can be obtained in a high degree of purity. Impure dichromate may readily be recrystallized from water and dried at 200° C. Under the right conditions of acidity, potassium dichromate is very satisfactory as a standard substance. The reaction first passes through an induction period and then proceeds at increasing speed. The acidity of the solution, to a great extent, controls the reaction. If, for instance, the acidity is in the neighborhood of 0.5–1.0 normal, it is necessary to let the solution

[6] W. C. Vosburgh, *J. Am. Chem. Soc.* 44, 2120 (1922).

[7] H. H. Willard and Philena Young, *J. Ind. Eng. Chem., Anal. Ed.* 7, 57 (1935).

[8] W. C. Bray and H. E. Miller, *J. Am. Chem. Soc.* 46, 2204 (1924).

[9] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* 17, 756 (1925).

stand for 5 minutes before titrating; but, if the acidity is 1.4 to 1.5 normal, the solution may be titrated immediately. However, the acidity must not be too high, otherwise, the possibility of air oxidation enters, which may lead to erroneous results. It is, therefore, extremely important to adjust the acidity to the right concentration, if correct results are to be obtained.

The practice of weighing out potassium dichromate, diluting to a specific volume, and assuming this to be exactly 0.1 normal, although sufficiently accurate for routine procedure, should not be acceptable for accurate work.

Weigh 0.12–0.15 gm of previously dried dichromate and dissolve in 50 cc of distilled water. Add 15 cc of 15% KI, and 7 cc of concentrated HCl. Titrate immediately and add starch as an indicator. The end point should be observed carefully so as not to overtitrate. The color change is from blue to the green color of chromic salts.

An alternate procedure may be used. Weigh out the sample and dissolve in 75 cc H_2O. Add 15 cc of 15% KI and 10 cc of concentrated HCl. Let stand for 5 minutes in the dark, dilute to 400 cc, and titrate.

Reaction:

$$K_2Cr_2O_7 + 6KI + 14HCl \longrightarrow 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$

Calculations: The equivalent weight of $K_2Cr_2O_7$ is 49.04

$$\text{Normality} = \frac{\text{Wt. of } K_2Cr_2O_7}{0.04904 \times \text{Titration in cc}}$$

Standardization with Copper or a Copper Salt

Copper of known purity, or a pure copper salt may be used as a standard substance. If copper is used, it should first be washed with alcohol and ether, to remove any oily material, polished bright with a suitable cleaner, rinsed with water, and again with alcohol, and finally dried for a short time at 105° C. Dissolve a suitable amount of the copper in 10 cc of 6 N H_2SO_4. Dilute to 35 cc with distilled water, add 15 cc of 15% KI, and titrate, using starch as an indicator. If the copper salt is used, dissolve the sample in 35 cc of distilled water, containing 5 cc of 6 N H_2SO_4. Add 15 cc of 15% KI, and titrate.

In a recent article, Huerre [10] states that a large excess of potassium iodide must be present. Loss of CuI is due to the solubility in thiosulphate solution.

G. Bruhns [11] found that potassium thiocyanate was useful in this titration, reducing the amount of potassium iodide necessary and speeding up the reaction. Kolthoff [12] gives the following procedure using thiocyanate: 0.5 to 1 cc of N KI is added to the acidified copper solution, and then 10 cc of 10% potassium thiocyanate. Cupric thiocyanate is precipitated. The solution is titrated immediately. The dark brown thio-

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[10] R. Huerre, *J. Pharm. Chim.* **23**, 594 (1936).
[11] G. Bruhns, *Chem. Ztg.* **42**, 301 (1918).
[12] Kolthoff and Furman, *Volumetric Analysis, Vol. II* (1929), p. 430.

cyanate disappears, while the solution assumes the dark brown color due to iodine. Toward the end, starch is added and the titration continued to a permanent change of iodine-starch blue to leather yellow or dirty violet.

Reaction: $2CuSO_4 + 4KI \longrightarrow 2K_2SO_4 + Cu_2I_2 + I_2$

Calculations: The equivalent weight of copper is 63.57, and that of $CuSO_4$ is 160.63.

$$\text{Normality} = \frac{\text{Wt. of Cu, or } CuSO_4}{\text{Milliequivalent} \times \text{cc Titration}}$$

Note: Much has been written concerning the stability [13, 14, 15] of thiosulphate solutions. Borax or sodium carbonate may be used as stabilizing agents, 0.1 gm Na_2CO_3 per liter, or 3.8 gm borax per liter. It has been the writer's experience that thiosulphate made up to volume with previously boiled distilled water and kept in clear glass bottles, in the dark, shows no appreciable diminution in titer, after 1–2 months. On the other hand, solutions kept in brown glass bottles gave evidence of deterioration within two weeks. When stabilized with either borax or carbonate, however, they retained their titer for longer periods.

Standardization of Potassium Permanganate

Molecular Weight: 158.03 $KMnO_4$
Equivalent Weight: 31.61

Preparation of the Solution

Analytical-grade potassium permanganate [16] may be used, or, to insure greater purity, since even the ana-

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[13] F. O. Rice, M. Kilpatrick, and W. Lemkin, *J. Am. Chem. Soc.* **45**, 1361 (1923).

[14] Kolthoff and Furman, *Volumetric Analysis, Vol. I* (1929), p. 231.

[15] Ph. Korkheimer, *Pharm. Ztg.* **80**, 1330 (1935).

[16] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **18**, 759 (1926).

lytical grade contains impurities, the salt may be recrystallized. Weigh out the required amount and dissolve in distilled water. Let the solution stand on the steam bath for 2–3 hours, or bring to a boil and heat 1 hour on the steam bath. This is necessary, since distilled water usually contains reducing substances. The solution is cooled and filtered either through a Gooch crucible or through a glass filtering funnel of the Büchner type having a porous plate. The manganese dioxide must be removed, since it acts as a catalytic agent, promoting the reduction of the permanganate. Make the filtered solution up to one liter, and transfer to a clean, clear glass bottle. Keep protected from the light. Some reduction will take place and, at intervals, it is necessary to filter off the manganese dioxide. Unless used constantly, it is best to restandardize before making a titration.

Standardization with Sodium Oxalate or Oxalic Acid

Sodium oxalate or oxalic acid purchased from the U. S. Bureau of Standards is recommended. Weigh out a 0.2–0.3 gm sample and dissolve in 50–60 cc of distilled water. Add 10 cc of 3 N H_2SO_4, heat to 80° C or a little above, and titrate slowly with permanganate. Do not let the temperature fall below 80° C. The reaction starts very slowly at first, and it is best to add only a few drops of permanganate. When some oxidation has taken place resulting in the formation of manganous salt, the reaction goes rapidly, due to the

catalytic action of the manganous ions. The solution must be stirred rapidly throughout the determination. The end point is taken as the first permanent pink coloration. In their standardization of permanganate with sodium oxalate, Fowler and Bright[17] correct for this error of overtitration, which they state to be 0.03–0.05 cc.

The presence of hydrochloric acid tends to give high results, due to oxidation of chloride ions to hypochlorous acid.

The reaction of permanganate, which is attended by side reactions, in its simplest form is as follows:

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Na_2SO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2\uparrow$$

or

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2\uparrow$$

Calculations: The equivalent weight of sodium oxalate is 66.995, and that of oxalic acid, with two molecules of water, 63.03

$$\text{Normality} = \frac{\text{Wt. of sample}}{0.067 \text{ (or } 0.06303) \times \text{cc Titration}}$$

Ammonium oxalate,[19] also, has been suggested as a primary standard.

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[17] R. M. Fowler & H. A. Bright, *J. Research Nat. Bur. Standards* 15, 493 (1935).

[18] Treadwell and Hall, *Analytical Chemistry, Vol. II* (1930), 513.

[19] M. M. Kirilov, *J. Applied Chem.* 9, 2067 (in French) (1936).

Standardization with Potassium Iodide

The principle of this method depends upon the following equation:

$$5KI + 2KMnO_4 + 16HCl \longrightarrow 7KCl + 2MnCl_2 + 5ICl + 8H_2O$$

Andrews[20] found that potassium iodide could be oxidized quantitatively by various reagents to colorless ICl, and also, that unless the acid concentration was fairly high, hydrolysis of the ICl took place. Kolthoff, Laitinen and Lingane,[21] who have applied this method to the standardization of permanganate, give the following procedure:

To a glass-stoppered flask containing 25 cc of distilled water and 1 cc of concentrated HCl, add pure potassium bicarbonate to slight excess. A weighed sample of fused potassium iodide is next added, and then sufficient concentrated HCl, assuming a final volume of 350 cc, so that the solution is 3.7–5.5 *N* with respect to the acid. Cool in an ice bath and add 6 cc CCl_4. Titrate with permanganate to the disappearance of the iodine color in the CCl_4 layer.

Calculations: $\text{Normality} = \dfrac{\text{Wt. of KI}}{0.08299 \times \text{cc Titration}}$

Note: Instead of the fused salt, potassium iodide, which has been dried at 200–220° C, may be used. The results may be slightly higher (0.02–0.03%) due to the retention of occluded water.

[20] L. W. Andrews, *J. Am. Chem. Soc.* **25**, 756 (1903); *Z. anorg. allgem. Chem.* **36**, 76 (1903).

[21] I. M. Kolthoff, H. A. Laitinen and J. J. Lingane, *J. Am. Chem. Soc.* **59**, 429 (1937).

Standardization with Iron Wire,[18] Ferrous Sulphate, or Mohr's Salt

A suitable quantity of pure iron wire, or either of the two salts is weighed out and dissolved in dilute sulphuric acid. The solution is diluted to approximately 100 cc and run through a Jones reductor, to insure complete reduction of the ion. Add 5 cc of phosphoric acid (85%) and titrate with permanganate to the first permanent pink color. The advantage of adding phosphoric acid is that colorless complex phosphate ions are formed, and the end point is, therefore, sharper, since otherwise it is a reddish orange.

Reactions:

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

$$10FeSO_4(NH_4)_2SO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10(NH_4)_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

Calculations:

The equivalent weights used are:

$$Fe = 55.84$$

$$FeSO_4 \cdot 7H_2O = 278.01$$

$$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O = 391.90$$

$$\text{Normality} = \frac{\text{Wt. of sample}}{\text{Milliequivalent} \times \text{cc Titration}}$$

Pure iron (electrolytic) is available for standardization. Mohr's salt, which has the advantage of a high equivalent weight, is seldom obtainable pure. However, the salt may still be used as a standard, if first its reducing power is determined.

Standardization of Potassium Dichromate

Molecular Weight: 294.21 $K_2Cr_2O_7$
Equivalent Weight: 49.04

Preparation of the Solution

Potassium dichromate, as previously stated, may be prepared to such a high degree of purity that many authors recommend weighing out the required amount of the salt and making up to volume, without further standardization.

Standardization with 0.1 N Sodium Thiosulphate

Pipette 25 cc of the dichromate solution to be standardized into a 300 cc Erlenmeyer flask. Add 15 cc of 15% KI solution and 7 cc of concentrated HCl. Titrate immediately with thiosulphate, using starch as an indicator. The color change is from blue to the characteristic green of chromic salts. This procedure has been dealt with under the standardization of thiosulphate.

Reaction:

$$K_2Cr_2O_7 + 6KI + 14HCl \longrightarrow 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

Calculations: $N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7} = N_{Thio} \times V_{Thio}$

Standardization with Ferrous Ammonium Sulphate

Potassium dichromate may also be standardized by use of ferrous ammonium sulphate [22] as a primary

[22] Recommended Specifications for Analytical Reagent Chemicals, *Ind. Eng. Chem.* **18**, 759 (1926).

standard. Sufficient amount of the purest obtainable salt is weighed out to give a titration of 35–40 cc. The titration may be carried out with either an outside indicator, potassium ferricyanide, or an internal indicator such as diphenylamine,[23] or diphenylbenzidine.[24, 25] If ferricyanide is used, a 0.01% solution is spotted on a porcelain plate, the ferrous ammonium sulphate is dissolved in 25 cc of distilled water, 10 cc of dilute H_2SO_4 added, and titrated with potassium dichromate. When the end point is near, the solution is spotted at intervals of 0.1 cc. The end point is reached when no blue color appears on the spot plate after two minutes.

If diphenylamine or diphenylbenzidine is used, it is necessary to add phosphoric acid either at the beginning of the titration or shortly before the true end point is reached. Phosphoric acid is necessary, since if it is not used, the end point is reached too soon, due to the indicator being partially oxidized by ferric ions. Phosphoric acid forms complexes with ferric ions, lowering the oxidation potential of the ferrous-ferric system. An indicator blank should be run, and the titration subtracted from the total titration of the sample.

Dissolve the sample in 25 cc of distilled water, add

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[23] J. Knop, *J. Am. Chem. Soc.* 46, 263 (1924).
[24] H. H. Willard and Philena Young, *J. Ind. Eng. Chem.* 20, 764 (1928).
[25] W. H. Cone and L. C. Cady, *J. Am. Chem. Soc.* 49, 357 (1927).

10 cc of dilute H_2SO_4 and 15 cc of sulphuric acid-phosphoric acid mixture (150 cc conc. H_2SO_4 and 160 cc 85% phosphoric acid made up to one liter). Add 2–3 drops of 1% indicator solution (in concentrated H_2SO_4) and titrate. As the end point approaches, the solution turns greenish blue and at the end point suddenly changes to an intense blue color.

Reaction: $K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4(NH_4)_2SO_4 \longrightarrow$
$K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + 7H_2O$

Calculations: The equivalent weight of ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ (Mohr's salt) is 391.90

$$\text{Normality} = \frac{\text{Wt. of sample}}{0.3919 \times \text{net cc Titration}}$$

Standardization of Ferrous Ammonium Sulphate, or Ferrous Sulphate

Molecular Weight: 391.90 Equivalent Weight: 391.90	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
Molecular Weight: 278.01 Equivalent Weight: 278.01	$FeSO_4 \cdot 7H_2O$

Preparation of the Solution

Ferrous ammonium sulphate—Mohr's salt—possesses the advantage of a high equivalent weight and the disadvantage in that it often contains small amounts of impurities. This, in spite of its high reacting weight, prevents it from being an ideal primary standard for oxidimetry. However, with regard to a standard solu-

tion of the salt, this does not present any difficulty, since it is only necessary to weigh slightly more than the theoretical amount to compensate for these impurities.

Mohr's salt and ferrous sulphate are subject to air oxidation, and both effloresce. They should be kept in tightly stoppered bottles. To overcome these difficulties, various methods have been used in preparing the pure salts. Kolthoff [26] suggests using ferric ammonium sulphate and reducing the solution with hydrogen sulphide. The crystallized ferrous ammonium sulphate is dried to constant weight over saturated sodium bromide solution. It is also possible to reduce ferric ammonium sulphate in a Jones reductor just before standardization. Kolthoff [27] states that ferric ammonium sulphate weathers readily but is stable at a relative humidity of 70%. Therefore, if this salt is used as a starting point, it is first necessary to allow it to come to equilibrium at 70% relative humidity.

If the commercial salts are used in the preparation of tenth normal solutions, 40 gm of Mohr's salt or 28 gm of ferrous sulphate are weighed, dissolved in 300 cc of distilled water containing 30 cc of concentrated sulphuric acid, and made up to one liter.

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[26] I. M. Kolthoff, *Pharm. Weekblad* 61, 561 (1926).

[27] Kolthoff and Furman, *Volumetric Analysis, Vol. II* (John Wiley, 1929), 294.

Standardization with Tenth Normal Potassium Dichromate

Pipette 25 cc of freshly prepared solution into a 250 cc Erlenmeyer flask. Add 10 cc of dilute sulphuric acid and 15 cc of sulphuric acid-phosphoric acid mixture (150 cc of conc. sulphuric acid, 160 cc of 85% phosphoric acid made up to one liter). Add 2–3 drops of indicator (1% solution of diphenylamine or diphenylbenzidine in concentrated sulphuric acid) and titrate with standard dichromate to the appearance of a deep blue end point. A blank titration should be run on the indicator and subtracted from the total titration.

Reaction:

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4(NH_4)_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + 7H_2O$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

Calculations: $N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7} = N_{\text{Mohr's Salt}} \times V_{\text{Mohr's Salt}}$

$$N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7} = N_{FeSO_4} \times V_{FeSO_4}$$

Note: The explanation of the use of phosphoric acid is given under the standardization of potassium dichromate.

Standardization with Tenth Normal Potassium Permanganate

Pipette 25 cc of ferrous ammonium sulphate or ferrous sulphate solution into a 250 cc Erlenmeyer flask. Add 25 cc of distilled water, 10 cc of dilute sulphuric acid, and 15 cc of sulphuric acid-phosphoric acid mixture. Titrate with previously standardized

tenth normal permanganate to the appearance of the first permanent pink color.

Reaction: $2KMnO_4 + 8H_2SO_4 + 10FeSO_4(NH_4)_2SO_4 \longrightarrow$
$K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + 8H_2O$

$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

Calculations: $N_{KMnO_4} \times V_{KMnO_4} = N_{Mohr's\ Salt} \times V_{Mohr's\ Salt}$

$N_{KMnO_4} \times V_{KMnO_4} = N_{FeSO_4} \times V_{FeSO_4}$

Standardization of Arsenious Oxide

Molecular Weight: 197.82 As_2O_3
Equivalent Weight: 49.46

Preparation of the Solution

Arsenic trioxide in pure form may be obtained from the Bureau of Standards. Weigh out 4.946 gm of arsenious oxide and dissolve in 250 cc of distilled water, containing 50 cc of normal sodium hydroxide. When solution has taken place, add enough acid, either hydrochloric or sulphuric, until the solution is neutral or faintly acid. Other methods dissolve arsenic trioxide in water containing sodium carbonate. The control of the final *p*H is important, since if the solution is too alkaline, the arsenite is more or less easily oxidized to arsenate, which naturally affects the titer. Tannanaev [28] states, however, that if the *p*H is kept between 7 and 9, the solution will keep indefinitely.

[28] N. A. Tannanaev, *Ukrainskii Khem. Zhurnal* 5, Sci. Pt. 217 (1930); *Chemical Abstracts* 25, 2070 (1931).

Standardization with Iodine

Pipette 25 cc of solution into an Erlenmeyer flask containing 25 cc of distilled water in which 1 gm of sodium bicarbonate has been dissolved. Titrate with standard iodine to the appearance of a blue color, using starch as an indicator. Sodium bicarbonate keeps the *p*H of the solution at about 8.36.

Reaction: $Na_3AsO_3 + I_2 + H_2O \longrightarrow Na_3AsO_4 + 2HI$

Calculations: $N_{As_2O_3} \times V_{As_2O_3} = N_{I_2} \times V_{I_2}$

Standardization of Potassium Bromate

Molecular Weight: 167.02 $KBrO_3$
Equivalent Weight: 27.84

Preparation of the Solution

Weigh out 2.784 gm of potassium bromate, previously dried at 150° C, dissolve in a small quantity of distilled water, and dilute to one liter.

Standardization with 0.1 N Sodium Thiosulphate

Pipette 25 cc of the bromate solution into a glass-stoppered bottle or iodine flask and add 20 cc of 10% sulphuric acid saturated with potassium bromide. Restopper the flask quickly and let stand for two minutes. Now add 5 cc of saturated potassium iodide solution, let stand one minute and titrate with *N*/10 sodium thiosulphate, using starch as an indicator.

Reactions:

$$KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3Br_2 + 3H_2O$$

$$Br_2 + 2KI \longrightarrow 2KBr + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

Calculations: $N_{KBrO_3} \times V_{KBrO_3} = N_{Thio} \times V_{Thio}$

Standardization with Arsenious Acid

Pipette 25 cc of standard arsenious oxide into a 300 cc Erlenmeyer flask, add 30 cc of 1:1 hydrochloric acid and 0.5 gm of potassium bromide. Add 1–2 drops of methyl orange. Titrate with the bromate solution, constantly agitating the flask. The end point is approached slowly. The color change is from red to colorless or pale yellow. The indicator change is due to bleaching of the compound by free bromine.

Reaction: $KBrO_3 + 5KBr + 6HCl \longrightarrow 6KCl + 3Br_2 + 3H_2O$

$As_2O_3 + 2Br_2 + 3H_2O \longrightarrow As_2O_5 + 4HBr + H_2O$

Calculations: $N_{KBrO_3} \times V_{KBrO_3} = N_{As_2O_3} \times V_{As_2O_3}$

Standardization with Aniline

Aniline may be used as a standard for potassium bromate. Its reaction is similar to phenol, in that it forms a tri-brom compound. An appropriate quantity of freshly distilled aniline is weighed out and transferred to a glass-stoppered iodine flask containing 20 cc of 10% sulphuric acid saturated with potassium bromide. Add 50 cc of bromate solution, and let stand for five minutes. Now add 5 cc of saturated potassium iodide solution, let stand one minute, and titrate the iodine with sodium thiosulphate, using starch as an incator.

Reaction:

$KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3Br_2 + 3H_2O$

$C_6H_5NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3NH_2 + 3HBr$

Calculations: The equivalent weight of aniline is 15.50

$$\text{Normality} = \frac{\text{Wt. of aniline}}{0.0155 \times \text{net cc of } KBrO_3}$$

Note: Potassium bromate solution is sometimes made up with potassium bromide. In this case, 50 gm of bromide are added per liter.

Standardization of Potassium Iodate

Molecular Weight: 214.03 KIO_3
Equivalent Weight: 35.67

Preparation of the Solution

Potassium iodate may be obtained pure by recrystallization from water. After drying at 180° C, the exact equivalent weight may be accurately weighed out, and made up to volume. However, to avoid any uncertainty as to the purity of the potassium iodate, it is best to standardize the solution.

Standardization with Sodium Thiosulphate

Pipette 25 cc of potassium iodate into a glass-stoppered flask containing 20 cc of 10% sulphuric acid and 5 cc of saturated potassium iodide solution. The reaction proceeds rapidly, and the solution may be titrated, immediately, with standard thiosulphate solution, using starch as an indicator.

Reaction: $KIO_3 + 5KI + 3H_2SO_4 \longrightarrow 3I_2 + 3K_2SO_4 + 3H_2O$

$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$

Calculations: $N_{KIO_3} \times V_{KIO_3} = N_{Thio} \times V_{Thio}$

Standardization with Thallous Carbonate

Berry[29] has suggested the use of thallous carbonate as a primary standard for iodate solutions.

Weigh out 0.4–0.5 gm of the salt, dissolve in distilled water, and make strongly acid with concentrated HCl. Add 15 cc of saturated KI solution, and titrate the liberated iodine, using starch as an indicator.

Reaction: $Tl_2CO_3 + KIO_3 + 8HCl \longrightarrow 2TlCl_3 + KCl + ICl + 4H_2O + CO_2\uparrow$

$ICl + KI \longrightarrow KCl + I_2$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

Calculations: The equivalent weight of Tl_2CO_3 is 117.2

$$\text{Normality} = \frac{\text{Wt. } Tl_2CO_3}{0.1172 \times \text{cc Titration}}$$

Standardization of Ceric Sulphate

Molecular Weight: 332.25 $Ce(SO_4)_2$
Equivalent Weight: 332.25

Ceric sulphate is a powerful oxidizing agent, and has been offered as a substitute for permanganate in oxidation reactions. There are numerous advantages, chief among which is the comparative stability[30] of ceric sulphate solutions and the fact that there is no decomposition when oxidations with excess sulphate are carried out at boiling temperatures.

Ceric sulphate, as received from chemical supply

[29] A. J. Berry, *Analyst* 64, 27 (1939).
[30] N. H. Furman, *J. Am. Chem. Soc.* 50, 755 (1928).

houses, averages around 50% as ceric sulphate, the variation being due to the presence of rare earths as impurities, and the fact that the salt is not completely anhydrous. Ceric ammonium sulphate,

$$Ce(SO_4)_2.2(NH_4)_2\ SO_4.2H_2O,$$

whose purity is around 80%, is also used in place of anhydrous ceric sulphate.

Preparation of the Solution

Allowing the ceric sulphate to be 50%, weigh out a little more than twice the equivalent weight, or 67 gm for a tenth normal solution. Add 100 cc of water and 30 cc of concentrated H_2SO_4. Let the solution stand until the salt is dissolved, adding more water or heating, if necessary. Make up to one liter. The solution will be approximately tenth normal in ceric sulphate and one normal in sulphuric acid.

If ceric ammonium sulphate ($2H_2O$) is used, weigh out an equivalent quantity of the salt, depending upon its purity, and dissolve in the same manner as for ceric sulphate. Standard solutions of ceric sulphate may also be prepared by dissolving the oxide, CeO,[31] in dilute sulphuric acid.

Standardization with Oxalic Acid or Sodium Oxalate

Weigh out 0.25–0.30 gm of oxalate and dissolve in 100 cc of distilled water. Add 10 cc of 1:1 H_2SO_4. Heat to 90–95° C and titrate with the ceric sulphate

[31] H. H. Willard and Philena Young, *J. Am. Chem. Soc.* **50**, 1322 (1928).

solution. The solution may be titrated using the ceric sulphate as an indicator, the end point being taken as the first permanent yellow tinge. Orthoferrous-phenanthroline [32, 33, 34, 35] is a very satisfactory indicator. One drop of the indicator solution is added. The color change is from pink to blue.

Reactions:

$$2Ce(SO_4)_2 + Na_2C_2O_4 \longrightarrow Ce_2(SO_4)_3 + Na_2SO_4 + 2CO_2\uparrow$$

$$2Ce(SO_4)_2 + H_2C_2O_4 \longrightarrow Ce_2(SO_4)_3 + H_2SO_4 + 2CO_2\uparrow$$

Calculations: $\text{Normality} = \dfrac{\text{Wt. of oxalate}}{0.067 \times \text{cc Titration}}$ or

$$\text{Normality} = \frac{\text{Wt. of oxalic acid}}{0.06303 \times \text{cc Titration}}$$

Standardization with Arsenious Oxide

Either a standard solution of tenth normal arsenite or pure arsenic trioxide (obtainable from the Bureau of Standards) may be used. If the dry salt is used, weigh 0.20 gm samples and dissolve in a few cubic centimeters of normal sodium hydroxide. If a previously standardized solution of arsenite is used, pipette

[32] G. H. Walden, L. P. Hammett, and R. P. Chapman, *J. Am. Chem. Soc.* 53, 3908 (1931).

[33] Monograph, Ortho-phenanthroline, published by The G. Frederick Smith Chemical Co., 857 McKinley Ave., Columbus, Ohio, P. O. Box 2611, Station D.

[34] A. U. Kirsanov and U. M. Cherkasou, *Zavodskaya Lab.* 5, 143; *Bull. Soc. Chem.* (5), 3, 817; *Chemical Abstracts* 30, 4779 (1936).

[35] H. H. Willard and Philena Young, *J. Am. Chem. Soc.* 55, 3260 (1933).

25 cc into an Erlenmeyer flask. Either sulphuric or hydrochloric acid may be added. The solution must be strongly acid, otherwise cerous sulphate will precipitate, since it is not very soluble in dilute acid. Add 50–75 cc of distilled water and 20–25 cc of concentrated hydrochloric acid or an equivalent amount of sulphuric acid. If the reagent itself is used as the indicator, the solution, as previously stated, must be heated to around 100° C, since the intensity of color is much greater when hot, making the end point easier to observe. Also, in the absence of a catalyst such as iodine monochloride[36] or osmium tetroxide, the solution must be heated to promote a fast reaction. Ortho-phenanthroline ferrous complex may be used as an indicator, one drop of a 0.025% solution being sufficient.

Reaction:

$$Na_3AsO_3 + 2Ce(SO_4)_2 H_2O \longrightarrow Na_3AsO_4 + Ce_2(SO_4)_3 + H_2SO_4$$

Calculations: $\text{Normality} = \dfrac{\text{Wt. of } As_2O_3}{0.04946 \times \text{cc Titration}}$

or $N_{Ce(SO_4)_2} \times V_{Ce(SO_4)_2} = N_{As_2O_3} \times V_{As_2O_3}$

Standardization with Mohr's Salt or Ferrous Sulphate

Make an approximately tenth normal solution of either Mohr's salt or ferrous sulphate, and determine its strength by titration with a standard solution of potassium dichromate. This is necessary, since the composition of either salt cannot be depended upon.

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[36] E. H. Swift and C. H. Gregory, *J. Am. Chem. Soc.* **52**, 901 (1930).

Having determined the exact strength of the iron solution, pipette 25 cc into an Erlenmeyer flask, and make the volume up to 100 cc. Add 10 cc of 1:1 sulphuric acid, and titrate with ceric sulphate, using ortho-phenanthroline ferrous complex.

Reaction: $2FeSO_4 + 2Ce(SO_4)_2 \longrightarrow Fe_2(SO_4)_3 + Ce_2(SO_4)_3$

Calculations: $N_{Ce(SO_4)_2} \times V_{Ce(SO_4)_2} = N_{FeSO_4} \times V_{FeSO_4}$

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CHAPTER VIII

Miscellaneous Standard Solutions

UNDER this heading are grouped several solutions whose practical importance in the analytical laboratory —with the exception of Wijs and Hanus solutions—is slight. However, since they are used to some extent, they have been included in the list of standard solutions.

STANDARDIZATION OF WIJS' OR HANUS' SOLUTION

Both of these solutions are used to determine unsaturation in organic compounds. The active constituent of Wijs' solution is iodine monochloride, and that of Hanus' solution is iodine monobromide. Glacial acetic acid is used as the solvent. There is no necessity for the solutions to contain exact equivalents.

Preparation of the Solution

Weigh out approximately 12.7 gm of iodine, and dissolve in several hundred cubic centimeters of glacial acetic acid. The iodine will dissolve readily in the acetic acid, if it has been ground to a fine powder in a

mortar. Gentle heating in a covered flask will facilitate solution, but prolonged heating will result in an appreciable loss of iodine. When the iodine is in complete solution, an equivalent (approximately) of chlorine or bromine is added. In the case of Wijs' solution, chlorine is bubbled slowly into the solution until the color begins to change and becomes definitely lighter. Caution: iodine must always be in excess, and the final color should be a deep red brown. A little experience will dictate the approximate point at which to stop.

Hanus' solution is prepared by adding 6.6 cc of bromine (not bromine water) to the acetic acid solution of iodine. Both solutions are now approximately 0.2 normal with respect to the iodine, since iodine, chlorine, and bromine are all equivalent to each other. Keep the solutions in brown bottles and store in a cupboard. Even under these conditions, the solutions will change their titer.

Standardization of the Solution

It is not necessary to standardize the solution, but its strength in terms of tenth normal thiosulphate is usually determined.

Pipette 25 cc of either Wijs' or Hanus' solution into a 250 cc Erlenmeyer flask, add 15 cc of 15% potassium iodide, and titrate with thiosulphate, using starch as an indicator, to the disappearance of the blue color. Record this titer as the strength of the solution. In running determinations of iodine values, it is always

necessary to include a blank, since, as stated above, the titer will change over a period of time.

Standardization of Iodine Thiocyanate Solution

Iodine thiocyanate is also used to determine unsaturation in organic compounds. The solution is stable for a comparatively short time, and should be kept in the dark.

Preparation of the Solution

To 900 cc of C.P. benzol, add 50 cc of acetic anhydride and 50 cc of glacial acetic acid. Allow to stand in a dry, glass-stoppered bottle, in the dark for eight days. Add 15 gm of lead thiocyanate and 2 cc of liquid bromine. Shake vigorously, at frequent intervals, until the solution has become decolorized. During this period, keep the solution in the dark or away from any source of bright light. After the solution is decolorized, add 4–6 gm of iodine. As soon as the iodine dissolves, filter the solution rapidly into a dry, glass-stoppered bottle and store in the dark.

Standardization of the Solution

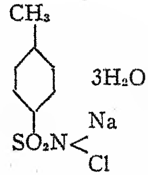
The strength of the solution is determined by titration with tenth normal thiosulphate.

Pipette 25 cc of the solution into a glass-stoppered iodine flask. Add quickly 15 cc of 15% potassium iodide, shake vigorously, and titrate the liberated iodine with tenth normal thiosulphate, using starch as an

indicator. A blank determination must always be run when determining unsaturation.

Standardization of Chloramine T

Molecular Weight: 281.5
Equivalent Weight: 140.75



Chloramine T—tolamine, activin—is the sodium salt of p-toluene sulphonchloroamide. Its use as a volumetric reagent [1, 2, 3, 4] was suggested by Noll.[5, 6] In its action, chloramine T resembles the hypochlorites and reacts in oxidation reactions similar to iodine. It has been used in determination of sulphites, arsenic, antimony, tin, and iron.

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[1] E. Jungmichl and J. Hackl, *Melliand Textilber.* **7**, 850 (1926).

[2] O. Tomicek and B. Sucharda, *Casopis Ceskoslov. Lekarnictva* **11**, 285, 309 (1931); *Chemical Abstracts* **26**, 1210 (1932).

[3] M. Markees, *Pharm. Acta Helv.* **6**, 106 (1931).

[4] A. S. Komarovskii, Vera Feodorovna Filanova, and I. M. Korenman, *J. Applied Chem.* (U.S.S.R.) **6**, 742 (1933); *Z. Anal. Chem.* **96**, 321 (1934).

[5] A. Noll, *Papier Fabr. Tech. Wiss. Teil* **22**, 385; *Zellstoff u. Papier* **4**, 218 (1924); *Chemical Abstracts* **19**, 176 (1925).

[6] A. Noll, *Chem. Ztg.* **48**, 845 (1924).

Preparation of the Solution

Since the purity of the commercial product may vary, approximately 15 gm are dissolved in water and made up to one liter (actually 14.1 gm represent one equivalent). If there are any doubts as to the purity, the salt may be recrystallized from water. The solution is stable,[7, 8] if kept in brown bottles.

Standardization with Arsenious Acid

Standardization may be made either with the dry salt or with a previously standardized solution of arsenious acid. Pipette 25 cc of tenth normal arsenious acid into an Erlenmeyer flask. Add 2–3 cc of a 10% solution of potassium iodide (or a small crystal), 5 cc of starch solution, and titrate to the first appearance of a blue color.

Calculations: $$N_{\text{Chlor.}} \times V_{\text{Chlor.}} = N_{As_2O_3} \times V_{As_2O_3}$$

or $$\text{Normality} = \frac{\text{Wt. of } As_2O_3}{0.04946 \times \text{cc Titration}}$$

Standardization of Hypochlorite Solutions

Hypochlorites and hypobromites are powerful oxidizing agents and useful in oxidation reactions that are carried out in alkaline or neutral solution. Kolthoff and Stenger [9] have proposed the use of calcium hypo-

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[7] Julius Bebie, *J. Am. Pharm. Assoc.* 9, 974 (1920).

[8] Bernard Salkin, *J. Am. Pharm. Assoc.* 13, 613 (1924).

[9] I. M. Kolthoff and V. A. Stenger, *Ind. Eng. Chem., Anal. Ed.* 7, 79 (1935).

chlorite as a standard reagent, since this compound is much more stable than the alkali hypochlorites. It may be obtained from the Mathieson Alkali Co., 60 East 42nd Street, New York City, under the code letters CCH.

Preparation of the Solution

Determine the available chlorine in the sample and weigh out enough to make a tenth normal solution when diluted to one liter. Store in a brown bottle, tightly stoppered. It will be necessary to recheck the titer of the solution, particularly if considerable time has elapsed since the solution was last used.

Standardization with Sodium Thiosulphate

Pipette 25 cc of the hypochlorite into an Erlenmeyer flask, and add 15 cc of a 15% solution of potassium iodide. Make up the volume to approximately 100 cc with distilled water, add 10 cc of concentrated hydrochloric acid, and titrate with thiosulphate to the disappearance of the blue color, using starch as an indicator.

Reactions:

$$Ca(OCl)_2 + 4KI + 4HCl \longrightarrow 4KCl + CaCl_2 + 2I_2 + 2H_2O$$

$$NaOCl + 2KI + 2HCl \longrightarrow 2KCl + NaCl + I_2 + H_2O$$

Equivalent weight in either case: $\dfrac{\text{Mol. Wt.}}{2}$

Calculations: $N_{OCl} \times V_{OCl} = N_{Thio} \times V_{Thio}$

Standardization with Arsenious Acid

Pipette 25 cc of the hypochlorite solution into a

250 cc Erlenmeyer flask. Add 50 cc of a tenth normal solution of arsenious acid. Titrate the excess arsenious acid with tenth normal iodine to the appearance of the blue starch-iodine color.

Calculations: Calculate the net cubic centimeters of arsenious acid used,

then,

$$N_{OCl} \times V_{OCl} = N_{As_2O_3} \times V_{As_2O_3}$$

A more recent addition to this type of standard oxidizing solution is the use of sodium chlorite as a volumetric oxidizing agent. Jackson and Parsons [10] have prepared and used it successfully for the determination of sulphurous acid and sulphites.

Standardization of Sodium Chlorite

Molecular Weight: 90.454 $NaClO_2$
Equivalent Weight: 22.614

Preparation of the Solution

Sodium chlorite is obtainable as a white crystalline solid, very soluble in water, slightly hygroscopic, and about 98% pure, the impurities consisting of sodium chloride, sodium chlorate, and water. The solution is stable over a period of several months, if kept in the dark. Weigh out the required amount of the salt, dissolve in distilled water, and make up to volume.

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[10] D. T. Jackson and J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.* 9, 14 (1937).

Standardization with Sodium Thiosulphate

Pipette 25 cc of the solution into an Erlenmeyer flask containing 75 cc of distilled water, 15 cc of 10% KI and 15 cc of 30% acetic acid. Titrate the liberated iodine with previously standardized thiosulphate solution, using starch as an indicator.

Reactions:

$$NaClO_2 + 4KI + 4CH_3COOH \longrightarrow NaCl + 4CH_3COOK + 2I_2 + 2H_2O$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Standardization of Titanium Trichloride or Sulphate

Molecular Weight:	154.27	$TiCl_3$
Equivalent Weight:	154.27	
Molecular Weight:	383.98	$Ti_2(SO_4)_3$
Equivalent Weight:	383.98	

Titanous salts are powerful reducing agents. As they are affected by air, the solutions are relatively unstable and must be kept under some inert gas. This necessitates special apparatus.[11] For isolated analyses, titanous solutions are not recommended. They find their usefulness, however, in routine work, where numerous determinations of the same sort are being run daily.

Preparation of the Solution

Concentrated solutions of the salts may be purchased.

[11] W. M. Thornton, Jr. and A. E. Ward, *J. Ind. Eng. Chem.* 19, 150 (1927).

From the strength of the solution, the volume which will contain an equivalent weight can be calculated. This is diluted with freshly boiled distilled water containing three per cent of concentrated hydrochloric acid (or equivalent of conc. H_2SO_4).

Standardization with Potassium Dichromate[11]

Pipette 25 cc of tenth normal dichromate into a 250 cc Erlenmeyer flask containing 50 cc of boiled distilled water and 5 cc of concentrated hydrochloric acid. Add several drops of diphenylamine as an indicator. Bubble carbon dioxide through the solution continuously and titrate with the titanous solution to an end point.

Reaction:

$$6TiCl_3 + K_2Cr_2O_7 + 14HCl \longrightarrow 6TiCl_4 + 2KCl + 2CrCl_3 + 7H_2O$$

Calculations: $N_{TiCl_3} \times V_{TiCl_3} = N_{K_2Cr_2O_7} \times V_{K_2Cr_2O_7}$

If the dry salt was used, then,

$$\text{Normality} = \frac{\text{Wt. of } K_2Cr_2O_7}{0.04903 \times \text{cc Titration}}$$

Equivalent weight of $K_2Cr_2O_7 = 49.03$

Note: The solution may also be standardized by titrating a sample of ferric ammonium sulphate (ferric alum), using 10 cc of 15% potassium thiocyanate as an indicator and titrating to the disappearance of the red ferric thiocyanate color. Follow the general directions as outlined under *Standardization.*

Standardization of Manganic Sulphate

Molecular Weight: 398.04 $Mn_2(SO_4)_3$
Equivalent Weight: 398.04

The use of manganic sulphate[12] as a standard re-

[12] A. R. Ubbelohde, *J. Chem. Soc.* 1605 (1935).

agent, in place of permanganate, presents interesting possibilities. Certain difficulties attendant to permanganate titration, such as the presence of chlorides, are overcome by manganic sulphate. A. R. Ubbelohde [12] states that satisfactory results have been obtained in the estimation of nitrites, oxalates, vanadium salts and hydrogen peroxide, and that rapid and satisfactory end points can be obtained without difficulty in the presence of chlorides.

Preparation of the Solution

According to Ubbelohde, a tenth normal solution may be prepared from manganous sulphate in the following manner, and according to the equation:

$$8MnSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow 5Mn_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

Dissolve 15.10 gm of manganous sulphate in 6 N H_2SO_4, and make up to a liter with 6 N H_2SO_4, keeping the solution cool. Now add 12 cc of $N/2$ $KMnO_4$, 2 cc at a time, at intervals of three minutes. A further 2 cc of concentrated H_2SO_4 were added after 8 cc and 12 cc of the $KMnO_4$ solution, and the solution stored four hours in the dark before use. With these precautions, the reaction proceeds smoothly. If larger volumes are required, special precautions must be taken for cooling the solution to prevent formation of precipitates of the higher oxides. This solution is stable at room temperature, but on dilution, unless the acid concentration is increased, hydrolysis will take place.

Standardization with Ferrous Ammonium Sulphate

Weigh out the necessary amount of ferrous ammonium sulphate and dissolve in 25 cc of distilled water. Add 10 cc of dilute H_2SO_4 and titrate. One drop excess of the reagent gives a definite pink color, which is greatly improved by addition of two drops of glacial phosphoric acid.

Reaction:

$$Mn_2(SO_4)_3 + 2FeSO_4(NH_4)_2SO_4 \longrightarrow 2MnSO_4 + Fe_2(SO_4)_3 + 2(NH_4)_2SO_4$$

Calculations: $\text{Normality} = \dfrac{\text{Wt. of } FeSO_4(NH_4)_2SO_4}{0.39804 \times \text{cc Titration}}$

Supplementary References

Calcium Chlorite as a Volumetric Oxidizing Agent, G. R. Levi, *Ind. Eng. Chem., Anal. Ed.* **9**, 250 (1937).

See also J. L. Parsons, *Ind. Eng. Chem., Anal. Ed.* **9**, 250 (1937).

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Oxidizing Action of Chloramine, T. G. Schiemann and P. Novak, *Z. Angew. Chem.* **40**, 1032 (1927).

The Oxidizing Power of Chloramines, J. Koetschet, P. Koetschet, and Pierre Viaud, *Helv. Chem. Acta* **13**, 587 (1930).

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Standardizing Titanous Chloride Solutions and Potentiometric Titration of Copper, E. Zintl and A Rauch. *Z. Anorg. Allgem. Chem.* **146**, 281 (1925).

Application of Titanous Chloride to Potentiometric Titrations, I. M. Kolthoff and O. Tomicek, *Rec. Trav. Chem.* **43**, 768 (1924).

Applied Inorganic Analysis, Hillebrand and Lundell (1929), 308.

Stock Solutions of Indicators

Acid-Base

Phenolphthalein: One gram dissolved in one liter of 50% alcohol. Alcohol is always faintly acid and must be first neutralized with 0.1*N* caustic before adding the indicator.

Methyl Orange: One gram dissolved in one liter of distilled water.

Methyl Yellow: 0.1% in alcohol.

Methyl Red: 0.1% in alcohol.

Thymol Blue: 0.1% in alcohol.

Oxidation-Reduction

Diphenylamine: 1% in conc. H_2SO_4.

Diphenylbenzidine: 1% in conc. H_2SO_4.

Ferrous *o*-phenanthroline: can be purchased* ready for use.

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* The G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio. P.O.B. 2611—Station D.

Precipitation

Ferric Ammonium Sulphate: Saturated solution in water. Enough concentrated HNO_3 added to clear the solution.

Ferric Nitrate: 10% solution in water.

Potassium Chromate: 5% solution in water.

Uranyl Acetate: 1% solution in water.

Stock Solutions of Laboratory Reagents

Concentrated Acids

Sulphuric acid	— 36 Normal
Hydrochloric acid	— 12 Normal
Nitric acid	— 16 Normal
Acetic acid	— 17.5 Normal
Hydrofluoric acid	— 48%
Aqua regia	— Mix 3 vols. of conc. HCl and 1 vol. conc. HNO_3 just before using.

Dilute Acids

Sulphuric acid	— 18 Normal. Dilute 460 cc of concentrated acid with 540 cc of distilled water.
Sulphuric acid	— 6 Normal. Dilute 1 vol. of concentrated acid with 5 vols. of distilled water.
Hydrochloric acid	— 6 Normal. Mix equal volumes of concentrated acid and distilled water.

Nitric acid	— 6 Normal. Dilute 380 cc of concentrated acid with 620 cc of distilled water.
Perchloric acid	— 2 Normal. Dilute 220 cc of 60% acid with 780 cc of distilled water.
Acetic acid	— 6 Normal. Dilute 350 cc of glacial acetic acid to one liter with distilled water.

Bases

Ammonium hydroxide	— 15 Normal. Concentrated. 6 Normal. Dilute 400 cc of concentrated ammonia with 600 cc of distilled water.
Sodium hydroxide	— 35%. Dissolve one pound of pellet caustic in 748 cc of distilled water.
Sodium hydroxide	— 5 Normal. Dissolve 220 gm in distilled water and make up to one liter.
Potassium hydroxide	— 5 Normal. Contains 312 gm per liter.

Miscellaneous Solutions

Ammonium chloride	— 5 Normal. Contains 268 gm per liter.
Ammonium nitrate	— Normal. Contains 80 gm per liter.

Ammonium oxalate	— 0.5 Normal. Contains 36 gm per liter.
Barium chloride	— 10%. 100 gm dissolved in 900 cc of distilled water.
Picric acid	— Saturated solution in distilled water.
Potassium iodide	— 15%. 150 gm dissolved in 850 cc of distilled water.
Silver nitrate	— 10%. 100 gm dissolved in 900 cc of distilled water.
Sodium carbonate	— 3 Normal. 159 gm per liter.
Stannous chloride	— Normal. 113 gm of $SnCl_2 \cdot 2H_2O$ per liter. The solution is made acid by addition of a few cubic centimeters of conc. HCl. To keep the solution reduced, strips of metallic tin should be added.

Normal Solutions of Acids and Bases

Compound	Formula	Molecular Weight	Normal Solution Contains gm/l	Milli-Equivalent gm/cc
Acetic Acid	CH_3COOH	60.03	60.03	0.06003
Boric Acid	H_3BO_3	61.84	61.84	0.06184
Hydrobromic Acid	HBr	80.92	80.92	0.08092
Hydrochloric Acid	HCl	36.46	36.46	0.03646
Oxalic Acid	$H_2C_2O_4$	126.05	53.03	0.05303
Phosphoric Acid	H_3PO_4	98.04	32.68	0.04902
Sulphuric Acid	H_2SO_4	98.08	49.04	0.04904
Ammonium Hydroxide	NH_4OH	17.03	17.03	0.01703
Barium Hydroxide	$Ba(OH)_2 8H_2O$	315.50	157.75	0.15775
Calcium Hydroxide	$Ca(OH)_2$	74.09	37.05	0.03705
Potassium Hydroxide	KOH	56.1	56.1	0.0561
Potassium Carbonate	K_2CO_3	138.20	69.10	0.06910
Sodium Carbonate	Na_2CO_3	106.00	53.00	0.05300
Sodium Hydroxide	NaOH	40.00	40.00	0.04000
Sodium Tetraborate	$Na_2B_4O_7$	201.43	100.72	0.10072
Sodium Tetraborate (Hydrated)	$Na_2B_4O_7 \cdot 10H_2O$	381.43	190.72	0.19072

Normal Solutions of Oxidizing and Reducing Agents

Compound	Formula	Molecular Weight	Normal Solution Contains gm/l	Milli-Equivalent gm/cc
Ammonium Oxalate	$(NH_4)_2C_2O_4 \cdot H_2O$	142.09	71.05	0.07105
Arsenious Acid	H_3AsO_3	125.93	62.97	0.06297
Arsenious Oxide	As_2O_3	197.82	49.46	0.04946
Bromine	Br	79.916	79.916	0.07992
Calcium Hypochlorite	$Ca(OCl)_2$	126.99	63.50	0.06350
Chlorine	Cl	35.457	35.457	0.03546
Ferrous Sulphate	$FeSO_4 \cdot 7H_2O$	278.02	278.02	0.27802
Ferrous Ammonium Sulphate	$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	392.14	392.14	0.39214
Hydrogen Peroxide	H_2O_2	34.02	17.01	0.01701
Hydrogen Sulphide	H_2S	34.08	17.04	0.01704
Iodine	I	126.92	126.92	0.12692
Oxalic Acid	$H_2C_2O_4$	90.036	45.018	0.04502
Oxalic Acid (Hydrated)	$H_2C_2O_4 \cdot 2H_2O$	126.05	63.03	0.06303
Potassium Bromate	$KBrO_3$	167.02	27.84	0.02784
Potassium Dichromate	$K_2Cr_2O_7$	294.21	49.04	0.04904
Potassium Iodate	KIO_3	214.03	35.67	0.03567
Potassium Permanganate	$KMnO_4$	158.03	31.61	0.03161
Sodium Thiosulphate	$Na_2S_2O_3$	158.11	158.11	0.15811
Sodium Thiosulphate (Hydrated)	$Na_2S_2O_3 \cdot 5H_2O$	248.19	248.19	0.24819
Sodium Oxalate	$Na_2C_2O_4$	133.99	66.995	0.067
Stannous Chloride	$SnCl_2$	189.61	94.80	0.0948
Stannous Chloride (Hydrated)	$SnCl_2 \cdot 2H_2O$	225.65	112.83	0.11283

Normal Solutions of Precipitating Agents

Compound	Formula	Molecular Weight	Normal Solution Contains gm/l	Milli-Equivalent gm/cc
Ammonium Thiocyanate	NH_4SCN	76.11	76.11	0.07611
Hydrochloric Acid	HCl	36.46	36.46	0.03646
Potassium Ferrocyanide	$K_4Fe(CN)_6$	368.26	368.26	0.36826
Potassium Ferrocyanide (hydrated)	$K_4Fe(CN)_6 \cdot 3H_2O$	422.33	422.33	0.42233
Potassium Thiocyanate	$KSCN$	97.17	97.17	0.09717
Silver Nitrate	$AgNO_3$	169.89	169.89	0.16989
Sodium Chloride	$NaCl$	58.45	58.45	0.05845

ACID-BASE

The weights of primary standards in the following tables are based on a titration of 40 cc of 0.1 N solution.

Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for $N/10$ Solutions
Guanidine Carbonate	Acid	180.18	0.09009	0.3604
Potassium Bicarbonate	Acid	100.11	0.10011	0.4004
Silver Chloride	HCl	143.34	0.14334	*
Sodium Carbonate	Acid	106.00	0.05300	0.2120
Sodium Tetraborate	Acid	201.43	0.10072	0.4029
Sodium Tetraborate (decahydrate)	Acid	381.43	0.19072	0.7629
Thallous Carbonate	Acid	468.79	0.23440	0.9376
Adipic Acid	Bases	146.14	0.07307	0.2923
Ammonium Acid Sulphate	Bases	115.11	0.11511	0.4604
Ammonium Triiodate	Bases	544.82	0.27241	1.0896
Benzoic Acid	Bases	122.12	0.12212	0.4885
Boric Acid	Bases	61.84	0.02061	0.0824
Mercuric Oxide	Bases	232.61	0.11630	0.4652
Oxalic Acid	Bases	126.05	0.05303	0.2121
Potassium Acid Phthalate	Bases	204.06	0.20406	0.8162
Potassium Biiodate	Bases	389.85	0.38985	1.5594
Salicylic Acid	Bases	138.12	0.06906	0.2762
Sodium Acid Phthalate	Bases	189.13	0.18913	0.7565
Succinic Acid	Bases	118.09	0.05905	0.2362
Sulfamic Acid	Bases	97.49	0.09749	0.3900

* Excess $AgNO_3$ solution.

Compound	Standard for	Moelcular Weight	Milli-Equivalent	Wt. in gm for $N/10$ Solutions
Ammonium Oxalate (monohydrate)	Permanganate Ceric Sulphate	142.09	0.07106	0.2842
Aniline	Potassium Bromate	93.12	0.01552	0.0621
Arsenious Oxide	Iodine Permanganate Ceric Sulphate	197.82	0.04946	0.1978
Calcium Oxalate	Permanganate Ceric Sulphate	128.08	0.06404	0.2562
Copper	Thiosulphate	63.57	0.06357	0.2543
Copper Oxide	Thiosulphate	79.57	0.07957	0.3183
Copper Sulphate	Thiosulphate Titanous Chloride Titanous Sulphate	160.63	0.16063	0.6425
Ferrous Ammonium Sulphate	Dichromate Permanganate	391.90	0.39190	1.5676
Ferrous Sulphate (heptahydrate)	Permanganate Dichromate	278.01	0.27801	1.1120
Hydrazine Sulphate	Iodine	130.12	0.03251	0.1300
Iodine	Arsenious Acid Thiosulphate	126.96	0.12692	0.5077
Iron	Permanganate	55.84	0.05584	0.2234
Oxalic Acid (dihydrate)	Permanganate	126.05	0.06303	0.2521
Potassium Biiodate	Thiosulphate	389.95	0.03249	0.1300
Potassium Bromate	Thiosulphate	167.02	0.02784	0.1114
Potassium Dichromate	Thiosulphate Titanous Chloride Titanous Sulphate Ferrous Ammonium Sulphate Ferrous Sulphate	291.21	0.04904	0.1962
Potassium Ferricyanide	Titanous Solutions	329.19	0.32919	1.3168

Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for $N/10$ Solutions
Potassium Ferrocyanide (trihydrate)	Permanganate	422.33	0.42233	1.6893
Potassium Iodate	Thiosulphate	214.03	0.03567	0.1427
Potassium Iodide	Thiosulphate Permanganate Ceric Sulphate	166.02	0.08301	0.3320
Potassium Oxalate (monohydrate)	Permanganate Ceric Sulphate	184.22	0.09211	0.3684
Potassium Permanganate	Ferrous Ammonium Sulphate Ferrous Sulphate	158.03	0.03161	0.1264
Silver Nitrate	Iodine	169.89	0.16989	0.6796
Sodium Bromate	Thiosulphate	150.91	0.02515	0.1006
Sodium Iodate	Thiosulphate	197.92	0.03299	0.1320
Sodium Oxalate	Permanganate Ceric Sulphate	133.99	0.0670	0.2680
Sodium Thiosulphate (pentahydrate)	Iodine Bromate Iodate	248.19	0.24819	0.9928
Thallous Carbonate	Iodate	468.78	0.1172	0.4688

PRECIPITATION

Compound	Standard for	Molecular Weight	Milli-Equivalent	Wt. in gm for $N/10$ Solutions
Ammonium Thiocyanate	Silver Nitrate	76.11	0.07611	0.3044
Potassium Thiocyanate	Silver Nitrate	97.17	0.09717	0.3887
Silver Nitrate	Thiocyanate	169.89	0.16989	0.6796
Sodium Chloride	Silver Nitrate	58.45	0.05845	0.2338
Zinc Oxide	Potassium Ferrocyanide	422.33	0.21117	0.8447

EQUATIONS INVOLVED IN STANDARDIZATION

Acid-Base

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$HCl + Na_2CO_3 \longrightarrow NaHCO_3 + NaCl$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2\uparrow$$

$$2HCl + Na_2B_4O_7 + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$$

$$HCl + AgNO_3 \longrightarrow AgCl + HNO_3$$

$$Tl_2CO_3 + 2HCl \longrightarrow 2TlCl + H_2O + CO_2\uparrow$$

$$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2HCl$$

$$NaOH + \begin{matrix} HOOC \diagdown \\ \qquad C_6H_4 \\ KOOC \diagup \end{matrix} \longrightarrow \begin{matrix} NaOOC \diagdown \\ \qquad C_6H_4 \\ KOOC \diagup \end{matrix} + H_2O$$

$$NaOH + KH(IO_3)_2 \longrightarrow KIO_3 + NaIO_3 + H_2O$$

Oxidation-Reduction

$$5(NH_4)_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5(NH_4)_2SO_4 + 8H_2O + 10CO_2\uparrow$$

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 8H_2O + 10CO_2\uparrow$$

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2\uparrow$$

$$H_3AsO_3 + I_2 + H_2O \longrightarrow H_3AsO_4 + 2HI$$

$$As_2O_3 + 2I_2 + 2H_2O \longrightarrow As_2O_5 + 4HI$$

$$Ca(OCl)_2 + 4HCl + 4KI \longrightarrow CaCl_2 + 2H_2O + 4KCl + 2I_2$$

$$Br_2 + 2KI + H_2SO_4 \longrightarrow 2KBr + H_2SO_4 + I_2$$

$$Cl_2 + 2KI + H_2SO_4 \longrightarrow 2KCl + H_2SO_4 + I_2$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

$$10FeSO_4(NH_4)_2SO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10(NH_4)_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

Oxidation-Reduction

$$5KI + 2KMnO_4 + 16HCl \longrightarrow 7KCl + 2MnCl_2 + 5ICl + 8H_2O$$

$$Mn_2(SO_4)_3 + 2FeSO_4(NH_4)_2SO_4 \longrightarrow 2MnSO_4 + Fe_2(SO_4)_3 + 2(NH_4)_2SO_4$$

$$2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$$

$$KIO_3 + 5KI + 6HCl \longrightarrow 6KCl + 3H_2O + 3I_2$$

$$KBrO_3 + 6KI + 6HCl \longrightarrow 6KCl + 3H_2O + 3I_2 + KBr$$

$$KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3Br_2 + 3H_2O$$

$$K_2Cr_2O_7 + 6KI + 14HCl \longrightarrow 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4(NH_4)_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + 7H_2O$$

$$SnCl_2 + I_2 + 2HCl \longrightarrow SnCl_4 + 2HI$$

$$2CuSO_4 + 4KI \longrightarrow 2K_2SO_4 + Cu_2I_2 + I_2$$

$$NaOCl + 2KI + 2HCl \longrightarrow 2KCl + NaCl + I_2 + H_2O$$

$$NaClO_2 + 4KI + 4CH_3COOH \longrightarrow NaCl + 4CH_3COOK + 2I_2 + 2H_2O$$

$$C_6H_5NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3NH_2 + 3HBr$$

$$2Ce(SO_4)_2 + Na_2C_2O_4 \longrightarrow Ce_2(SO_4)_3 + Na_2SO_4 + 2CO_2\uparrow$$

$$2Ce(SO_4)_2 + H_2C_2O_4 \longrightarrow Ce_2(SO_4)_3 + H_2SO_4 + 2CO_2\uparrow$$

$$2Ce(SO_4)_2 + Na_3AsO_3 + H_2O \longrightarrow Na_3AsO_4 + Ce_2(SO_4)_3 + H_2SO_4$$

$$2Ce(SO_4)_2 + 2FeSO_4 \longrightarrow Fe_2(SO_4)_3 + Ce_2(SO_4)_3$$

$$Tl_2CO_3 + KIO_3 + 8HCl \longrightarrow 2TlCl_3 + KCl + ICl + 4H_2O + CO_2\uparrow$$

$$6TiCl_3 + K_2Cr_2O_7 + 14HCl \longrightarrow 6TiCl_4 + 2KCl + 2CrCl_3 + 7H_2O$$

Precipitation

$$KSCN + AgNO_3 \longrightarrow AgSCN + KNO_3$$

$$NH_4SCN + AgNO_3 \longrightarrow AgSCN + NH_4NO_3$$

$$HCl + AgNO_3 \longrightarrow AgCl + HNO_3$$

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

$$2K_4Fe(CN)_6 + 3ZnSO_4 \longrightarrow K_2Zn_3[Fe(CN)_6]_2 + 3K_2SO_4$$

LOGARITHMS OF VOLUMETRIC FACTORS BASED ON THE VALUE OF A NORMAL SOLUTION

Acid-Base

Compound	Formula	Milli-Equiv-alent	Loga-rithm
Ammonium Hydroxide	NH_4OH	0.03505	$\bar{2}.54469$
Barium Hydroxide	$Ba(OH)_2$	0.08569	$\bar{2}.93293$
Hydrochloric Acid	HCl	0.036465	$\bar{2}.56189$
Potassium Acid Phthalate	$KHO_4C_8H_4$	0.20406	$\bar{1}.30976$
Potassium Biiodate	$KH(IO_3)_2$	0.3899	$\bar{1}.59095$
Potassium Hydroxide	KOH	0.05610	$\bar{2}.74896$
Silver Chloride	$AgCl$	0.14334	$\bar{1}.15637$
Sodium Tetraborate	$Na_2B_4O_7$	0.10072	$\bar{1}.00312$
Sodium Tetraborate (Hydrated)	$Na_2B_4O_7 \cdot 10H_2O$	0.19072	$\bar{1}.28040$
Sodium Carbonate	Na_2CO_3	0.0530	$\bar{2}.72428$
Sodium Hydroxide	$NaOH$	0.0400	$\bar{2}.60206$
Sulphuric Acid	H_2SO_4	0.04904	$\bar{2}.69055$

LOGARITHMS OF VOLUMETRIC FACTORS BASED ON THE VALUE OF A NORMAL SOLUTION

Oxidation-Reduction

Compound	Formula	Milli-Equivalent	Logarithm
Arsenious Acid	As_2O_3	0.04946	$\bar{2}.69425$
Calcium Hypochlorite	$Ca(OCl)_2$	0.06350	$\bar{2}.80277$
Ceric Sulphate	$Ce(SO_4)_2$	0.33225	$\bar{1}.52147$
Chloramine T	$p\text{-}C_6H_4CH_3SO_2N\genfrac{}{}{0pt}{}{\diagup Na}{\diagdown Cl}$	0.14075	$\bar{1}.14845$
Copper	Cu	0.06357	$\bar{2}.80325$
Copper Sulphate	$CuSO_4$	0.15963	$\bar{1}.20311$
Ferrous Ammonium Sulphate (Mohr's Salt)	$FeSO_4 \cdot (NH_4)_2\text{-}SO_4 \cdot 6H_2O$	0.39190	$\bar{1}.59318$
Ferrous Sulphate	$FeSO_4 \cdot 7H_2O$	0.27801	$\bar{1}.44406$
Iodine	I	0.12692	$\bar{1}.10353$
Oxalic Acid	$H_2C_2O_4 \cdot 2H_2O$	0.06303	$\bar{2}.79955$
Potassium Bromate	$KBrO_3$	0.02784	$\bar{2}.44467$
Potassium Dichromate	$K_2Cr_2O_7$	0.04904	$\bar{2}.69055$
Potassium Iodate	KIO_3	0.03567	$\bar{2}.55230$
Potassium Permanganate	$KMnO_4$	0.03161	$\bar{2}.49982$
Sodium Hypochlorite	NaOCl	0.037227	$\bar{2}.57086$
Sodium Oxalate	$Na_2C_2O_4$	0.066995	$\bar{2}.82604$
Sodium Thiosulphate	$Na_2S_2O_3$	0.15811	$\bar{1}.19896$
Sodium Thiosulphate (Hydrated)	$Na_2S_2O_3 \cdot 5H_2O$	0.24819	$\bar{1}.39478$
Titanium Chloride	$TiCl_3$	0.15427	$\bar{1}.18828$
Titanium Sulphate	$Ti_2(SO_4)_3$	0.38398	$\bar{1}.58431$

Precipitation

Compound	Formula	Milli-Equivalent	Logarithm
Ammonium Thiocyanate	NH_4SCN	0.07611	$\bar{2}.88144$
Potassium Ferrocyanide	$K_4Fe(CN)_6 \cdot 3H_2O$	0.21117	$\bar{1}.32463$
Potassium Thiocyanate	$KSCN$	0.09717	$\bar{2}.98753$
Silver Nitrate	$AgNO_3$	0.16989	$\bar{1}.23017$
Sodium Chloride	$NaCl$	0.05845	$\bar{2}.76678$

ABSOLUTE DENSITY OF WATER *

This table gives the weight in grams of a cubic centimeter of water at temperatures from 0° to 30°C. Water attains its maximum density at 3.98°C. at which temperature the density is 0,999973 (C. G. S.)

Temp. °C.	Density	Temp. °C.	Density	Temp. °C.	Density	Temp. °C.	Density
0.0	0.999841	7.6	0.999872	15.2	0.999069	22.8	0.997585
0.2	9854	7.8	9861	15.4	9038	23.0	7538
0.4	9866	8.0	9849	15.6	9007	23.2	7490
0.6	9878	8.2	9837	15.8	8975	23.4	7442
0.8	9889	8.4	9824	16.0	8943	23.6	7394
1.0	9900	8.6	9810	16.2	8910	23.8	7345
1.2	9909	8.8	9796	16.4	8877	24.0	7296
1.4	9918	9.0	9781	16.6	8843	24.2	7246
1.6	9927	9.2	9766	18.8	8809	24.4	7196
1.8	9934	9.4	9751	17.0	8774	24.6	7146
2.0	9941	9.6	9734	17.2	8739	24.8	7095
2.2	9947	9.8	9717	17.4	8704	25.0	7044
2.4	9953	10.0	9700	17.6	8668	25.2	6992
2.6	9958	10.2	9682	17.8	8632	25.4	6941
2.8	9962	10.4	9664	18.0	8595	25.6	6888
3.0	9965	10.6	9645	18.2	8558	25.8	6836
3.2	9968	10.8	9625	18.4	8520	26.0	6783
3.4	9970	11.0	9605	18.6	8482	26.2	6729
3.6	9972	11.2	9585	18.8	8444	26.4	6676
3.8	9973	11.4	9564	19.0	8405	26.6	6621
4.0	9973	11.6	9542	19.2	8365	26.8	6567
4.2	9973	11.8	9520	19.4	8325	27.0	6512
4.4	9972	12.0	9498	19.6	8285	27.2	6457
4.6	9970	12.2	9475	19.8	8244	27.4	8401
4.8	9968	12.4	9451	20.0	8203	27.6	6345
5.0	9965	12.6	9427	20.2	8152	27.8	6289
5.2	9961	12.8	9402	20.4	8120	28.0	6232
5.4	9957	13.0	9377	20.6	8078	28.2	6175
5.6	9952	13.2	9352	20.8	8035	28.4	6118
5.8	9947	13.4	9326	21.0	7992	28.6	6060
6.0	9941	13.6	9299	21.2	7948	28.8	6002
6.2	9935	13.8	9272	21.4	7904	29.0	5944
6.4	8927	14.0	9244	21.6	7860	29.2	5885
6.6	9920	14.2	9216	21.8	7815	29.4	5826
6.8	9911	14.4	9188	22.0	7770	29.6	5766
7.0	9902	14.6	9159	22.2	7724	29.8	5706
7.2	9893	14.8	9129	22.4	7678	30.0	5646
7.4	9883	15.0	9099	22.6	7632		

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HYDRATION TEMPERATURES, MELTING POINTS, AND BOILING POINTS FOR CALIBRATION OF THERMOMETERS

Compound	Formula	Hydration Temperature
Sodium Chromate	$Na_2CrO_4 \cdot 10H_2O$	19.71° C
Sodium Sulphate	$Na_2SO_4 \cdot 10H_2O$	32.383
Sodium Carbonate	$Na_2CO_3 \cdot 7H_2O$	35.3
Sodium Thiosulphate	$Na_2S_2O_3 \cdot 5H_2O$	48.0
Sodium Bromide	$NaBr \cdot 2H_2O$	50.8
Manganese Chloride	$MnCl_2 \cdot 4H_2O$	57.8
Trisodium Phosphate	$Na_3PO_4 \cdot 12H_2O$	73.4
Barium Hydroxide	$Ba(OH)_2 \cdot 8H_2O$	78.0
		Melting Points
Naphthalene	$C_{10}H_8$	80.8° C
Phenanthrene	$(C_6H_4CH)_2$	101.0
Benzoic Acid	C_6H_5COOH	122.45
Salicylic Acid	$HO \cdot C_6H_4COOH$	159.8
Anisic Acid	$CH_3O \cdot C_6H_4 \cdot COOH$	184.2
Anthracene	$(C_6H_4CH)_2$	216.1
Carbazole	$C_6H_4NH \cdot C_6H_4$	247.0
Anthraquinone	$(C_6H_4)_2(CO)_2$	285.0
		Boiling Points @ 760 mm
Toluene	$C_6H_5CH_3$	110.5° C
Monochlorbenzene	C_6H_5Cl	132.1
Monobrombenzene	C_6H_5Br	156.2

References

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100 — 150

N.	L.	0	1	2	3	4	5	6	7	8	9
100	00	000	043	087	130	173	217	260	303	346	389
101		432	475	518	561	604	647	689	732	775	817
102		860	903	945	988	*030	*072	*115	*157	*199	*242
103	01	284	326	368	410	452	494	536	578	620	662
104		703	745	787	828	870	912	953	995	*036	*078
105	02	119	160	202	243	284	325	366	407	449	490
106		531	572	612	653	694	735	776	816	857	898
107		938	979	*019	*060	*100	*141	*181	*222	*262	*302
108	03	342	383	423	463	503	543	583	623	663	703
109		743	782	822	862	902	941	981	*021	*060	*100
110	04	139	179	218	258	297	336	376	415	454	493
111		532	571	610	650	689	727	786	805	844	883
112		922	961	999	*038	*077	*115	*154	*192	*231	*269
113	05	308	346	385	423	461	500	538	576	614	652
114		690	729	767	805	843	881	918	956	994	*032
115	06	070	108	145	183	221	258	296	333	371	408
116		446	483	521	558	595	633	670	707	744	781
117		819	856	893	930	967	*004	*041	*078	*115	*151
118	07	188	225	262	298	335	372	408	445	482	518
119		555	591	628	664	700	737	773	809	846	882
120		918	954	990	*027	*083	*099	*135	*171	*207	*243
121	08	279	314	350	386	422	458	493	529	565	600
122		636	672	707	743	778	814	849	884	920	955
123		991	*026	*061	*096	*132	*167	*202	*237	*272	*307
124	09	342	377	412	447	482	517	552	587	621	656
125		691	726	760	795	830	864	899	934	968	*003
126	10	037	072	106	140	175	209	243	278	312	346
127		380	415	449	483	517	551	585	619	653	687
128		721	755	789	823	857	890	924	958	992	*025
129	11	059	093	126	160	193	227	261	294	327	361
130		394	428	461	494	528	561	594	628	661	694
131		727	760	793	826	860	893	928	959	992	*024
132	12	057	090	123	156	189	222	254	287	320	352
133		385	418	450	483	516	548	581	613	646	678
134		710	743	775	808	840	872	905	937	969	*001
135	13	033	066	098	130	162	194	226	258	290	322
136		354	386	418	450	481	513	545	577	609	640
137		672	704	735	767	799	830	862	893	925	956
138		988	*019	*051	*082	*114	*145	*176	*208	*239	*270
139	14	301	333	364	395	426	457	489	520	551	582
140		613	644	675	706	737	768	789	829	860	891
141		922	953	983	*014	*045	*076	*106	*137	*168	*198
142	15	229	259	290	320	351	381	412	442	473	503
143		534	564	594	625	655	685	715	748	776	806
144		836	866	897	927	957	987	*017	*047	*077	*107
145	16	137	167	197	227	256	286	316	346	376	406
146		435	465	495	524	554	584	613	643	673	702
147		732	761	791	820	850	879	909	938	967	997
148	17	026	056	085	114	143	173	202	231	260	289
149		319	348	377	406	435	464	493	522	551	580
150		609	638	667	696	725	754	782	811	840	869
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	44	43	42	41	40	39	38	37	36	35	34	33	32	31	30
1	4.4	4.3	4.2	4.1	4.0	3.9	3.8	3.7	3.6	3.5	3.4	3.3	3.2	3.1	3.0
2	8.8	8.6	8.4	8.2	8.0	7.8	7.6	7.4	7.2	7.0	6.8	6.6	6.4	6.2	6.0
3	13.2	12.9	12.6	12.3	12.0	11.7	11.4	11.1	10.8	10.5	10.2	9.9	9.6	9.3	9.0
4	17.6	17.2	16.8	16.4	16.0	15.6	15.2	14.8	14.4	14.0	13.6	13.2	12.8	12.4	12.0
5	22.0	21.5	21.0	20.5	20.0	19.5	19.0	18.5	18.0	17.5	17.0	16.5	16.0	15.5	15.0
6	26.4	25.8	25.2	24.6	24.0	23.4	22.8	22.2	21.6	21.0	20.4	19.8	19.2	18.6	18.0
7	30.8	30.1	29.4	28.7	28.0	27.3	26.6	25.9	25.2	24.5	23.8	23.1	22.4	21.7	21.0
8	35.2	34.4	33.6	32.8	32.0	31.2	30.4	29.6	28.8	28.0	27.2	26.4	25.6	24.8	24.0
9	39.6	38.7	37.8	36.9	36.0	35.1	34.2	33.3	32.4	31.5	30.6	29.7	28.8	27.9	27.0

.00000 — .17869

150 — 200

N.	L.	0	1	2	3	4	5	6	7	8	9
150	17	609	638	667	696	725	754	782	811	840	869
151		898	926	955	984	*013	*041	*070	*099	*127	*156
152	18	104	213	241	270	298	327	355	384	412	441
153		469	498	526	554	583	611	639	667	696	724
154		752	780	808	837	865	893	921	949	977	*005
155	19	033	061	089	117	145	173	201	229	257	285
156		312	340	368	396	424	451	479	507	535	562
157		590	618	645	673	700	728	756	783	811	838
158		866	893	921	948	976	*003	*030	*058	*085	*112
159	20	140	167	194	222	249	276	303	330	358	385
160		412	439	466	493	520	548	575	602	629	656
161		683	710	737	763	790	817	844	871	898	925
162		952	978	*005	*032	*059	*085	*112	*139	*165	*192
163	21	219	245	272	299	325	352	378	405	431	458
164		484	511	537	564	590	617	643	669	696	722
165		748	775	801	827	854	880	906	932	958	985
166	22	011	037	063	089	115	141	167	194	220	246
167		272	298	324	350	376	401	427	453	479	505
168		531	557	583	608	634	660	686	712	737	763
169		789	814	840	866	891	917	943	968	994	*019
170	23	045	070	096	121	147	172	198	223	249	274
171		300	325	350	376	401	426	452	477	502	528
172		553	578	603	629	654	679	704	729	754	779
173		805	830	855	880	905	930	955	980	*005	*030
174	24	055	080	105	130	155	180	204	229	254	279
175		304	329	353	378	403	428	452	477	502	527
176		551	576	601	625	650	674	699	724	748	773
177		797	822	846	871	895	920	944	969	993	*018
178	25	042	066	091	115	139	164	188	212	237	261
179		285	310	334	358	382	406	431	455	479	503
180		527	551	575	600	624	648	672	696	720	744
181		768	792	816	840	864	888	912	935	959	983
182	26	007	031	055	079	102	126	150	174	198	221
183		245	269	293	316	340	364	367	411	435	458
184		482	505	529	553	576	600	623	647	670	694
185		717	741	764	788	811	834	858	881	905	928
186		951	975	998	*021	*045	*068	*091	*114	*138	*161
187	27	184	207	231	254	277	300	323	346	370	393
188		416	439	462	485	508	531	554	577	600	623
189		646	669	692	715	738	761	784	807	830	852
190		875	898	921	944	967	989	*012	*035	*058	*081
191	28	103	126	149	171	194	217	240	262	285	307
192		330	353	375	398	421	443	466	488	511	533
193		556	578	601	623	646	668	691	713	735	758
194		780	803	825	847	870	892	914	937	959	981
195	29	003	026	048	070	092	115	137	159	181	203
196		226	248	270	292	314	336	358	380	403	425
197		447	469	491	513	535	557	579	601	623	645
198		667	688	710	732	754	776	798	820	842	863
199		885	907	929	951	973	994	*016	*038	*060	*081
200	30	103	125	146	168	190	211	233	255	278	298
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	29	28	27	26	25	24	23	22	21
1	2.9	2.8	2.7	2.6	2.5	2.4	2.3	2.2	2.1
2	5.8	5.6	5.4	5.2	5.0	4.8	4.6	4.4	4.2
3	8.7	8.4	8.1	7.8	7.5	7.2	6.9	6.6	6.3
4	11.6	11.2	10.8	10.4	10.0	9.6	9.2	8.8	8.4
5	14.5	14.0	13.5	13.0	12.5	12.0	11.5	11.0	10.5
6	17.4	16.8	16.2	15.6	15.0	14.4	13.8	13.2	12.6
7	20.3	19.6	18.9	18.2	17.5	16.8	16.1	15.4	14.7
8	23.2	22.4	21.6	20.8	20.0	19.2	18.4	17.6	16.8
9	26.1	25.2	24.3	23.4	22.5	21.6	20.7	19.8	18.9

Proportional parts

.17 609 — .30 298

200 — 250

N.	L.	0	1	2	3	4	5	6	7	8	9
200	30	103	125	146	168	190	211	233	255	276	298
201		320	341	363	384	406	428	449	471	492	514
202		535	557	578	600	621	643	664	685	707	728
203		750	771	792	814	835	856	878	899	920	942
204		963	984	*006	*027	*048	*069	*091	*112	*133	*154
205	31	175	197	218	239	260	281	302	323	345	366
206		387	408	429	450	471	492	513	534	555	576
207		597	618	639	660	681	702	723	744	765	785
208		806	827	848	869	890	911	931	952	973	994
209	32	015	035	056	077	098	118	139	160	181	201
210		222	243	263	284	305	325	346	386	387	408
211		428	449	469	490	510	531	552	572	593	613
212		634	654	675	695	715	736	756	777	797	818
213		638	858	879	899	919	940	960	980	*001	*021
214	33	041	062	082	102	122	143	163	183	203	224
215		244	264	284	304	325	345	365	385	405	425
216		445	465	486	506	526	546	566	586	606	626
217		646	666	686	706	726	746	766	786	806	826
218		846	866	885	905	925	945	965	985	*005	*025
219	34	044	064	084	104	124	143	163	183	203	223
220		242	262	282	301	321	341	361	380	400	420
221		439	459	479	498	518	537	557	577	596	616
222		635	655	674	694	713	733	753	772	792	811
223		830	850	869	889	908	928	947	967	986	*005
224	35	025	044	064	083	102	122	141	160	180	199
225		218	238	257	276	295	315	334	353	372	392
226		411	430	449	468	488	507	526	545	564	583
227		603	622	641	660	679	698	717	736	755	774
228		793	813	832	851	870	889	908	927	946	965
229		984	*003	*021	*040	*059	*078	*097	*116	*135	*154
230	36	173	192	211	229	248	267	286	305	324	342
231		361	380	399	418	436	455	474	493	511	530
232		549	568	586	605	624	642	661	680	698	717
233		736	754	773	791	810	829	847	866	884	903
234		922	940	959	977	996	*014	*033	*051	*070	*088
235	37	107	125	144	162	181	199	218	236	254	273
236		291	310	328	346	365	383	401	420	438	457
237		475	493	511	530	548	566	585	603	621	639
238		658	676	694	712	731	749	767	785	803	822
239		840	858	876	894	912	931	949	967	985	*003
240	38	021	039	057	075	093	112	130	148	166	184
241		202	220	238	256	274	292	310	328	346	364
242		382	399	417	435	453	471	489	507	525	543
243		561	578	596	614	632	650	668	686	703	721
244		739	757	775	792	810	828	846	863	881	899
245		917	934	952	970	987	*005	*023	*041	*058	*076
246	39	094	111	129	146	164	182	199	217	235	252
247		270	287	305	322	340	358	375	393	410	428
248		445	463	480	498	515	533	550	568	585	602
249		620	637	655	672	690	707	724	742	759	777
250		794	811	829	846	863	881	898	915	933	950
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	22	21	20	19	18	17
1	2.2	2.1	2.0	1.9	1.8	1.7
2	4.4	4.2	4.0	3.8	3.6	3.4
3	6.6	6.3	6.0	5.7	5.4	5.1
4	8.8	8.4	8.0	7.6	7.2	6.8
5	11.0	10.5	10.0	9.5	9.0	8.5
6	13.2	12.6	12.0	11.4	10.8	10.2
7	15.4	14.7	14.0	13.3	12.6	11.9
8	17.6	16.8	16.0	15.2	14.4	13.6
9	19.8	18.9	18.0	17.1	16.2	15.3

Proportional parts

.30 103 — .59 950

N.	L. 0	1	2	3	4	5	6	7	8	9
250	39 794	811	829	846	863	881	898	915	933	950
251	967	985	*002	*019	*037	*054	*071	*088	*106	*123
252	40 140	157	175	192	209	226	243	261	278	295
253	312	329	346	364	381	398	415	432	449	466
254	483	500	518	535	552	569	586	603	620	637
255	654	671	688	705	722	739	756	773	790	807
256	824	841	858	875	892	909	926	943	960	976
257	993	*010	*027	*044	*061	*078	*095	*111	*128	*145
258	41 162	179	196	212	229	246	263	280	296	313
259	330	347	363	380	397	414	430	447	464	481
260	497	514	531	547	564	581	597	614	631	647
261	664	681	697	714	731	747	764	780	797	814
262	830	847	863	880	896	913	929	946	963	979
263	996	*012	*029	*045	*062	*078	*095	*111	*127	*144
264	42 160	177	193	210	226	243	259	275	292	308
265	325	341	357	374	390	406	423	439	455	472
266	488	504	521	537	553	570	586	602	619	635
267	651	667	684	700	716	732	749	765	781	797
268	813	830	846	862	878	894	911	927	943	959
269	975	991	*008	*024	*040	*056	*072	*088	*104	*120
270	43 136	152	169	185	201	217	233	249	265	281
271	297	313	329	345	361	377	393	409	425	441
272	457	473	489	505	521	537	553	569	584	600
273	616	632	648	664	680	696	712	727	743	759
274	775	791	807	823	838	854	870	886	902	917
275	933	949	965	981	996	*012	*028	*044	*059	*075
276	44 091	107	122	138	154	170	185	201	217	232
277	248	264	279	295	311	326	342	358	373	389
278	404	420	436	451	467	483	498	514	529	545
279	560	576	592	607	623	638	654	669	685	700
280	716	731	747	762	778	793	809	824	840	855
281	871	886	902	917	932	948	963	979	994	*010
282	45 025	040	056	071	086	102	117	133	148	163
283	179	194	209	225	240	255	271	286	301	317
284	332	347	362	378	393	408	423	439	454	469
285	484	500	515	530	545	561	576	591	606	621
286	637	652	667	682	697	712	728	743	758	773
287	788	803	818	834	849	864	879	894	909	924
288	939	954	969	984	*000	*015	*030	*045	*060	*075
289	46 090	105	120	135	150	165	180	195	210	225
290	240	255	270	285	300	315	330	345	359	374
291	389	404	419	434	449	464	479	494	509	523
292	538	553	568	583	598	613	627	642	657	672
293	687	702	716	731	746	761	776	790	805	820
294	835	850	864	879	894	909	923	938	953	967
295	982	997	*012	*026	*041	*056	*070	*085	*100	*114
296	47 129	144	159	173	188	202	217	232	246	261
297	276	290	305	319	334	349	363	378	392	407
298	422	436	451	465	480	494	509	524	538	553
299	567	582	596	611	625	640	654	669	683	698
300	712	727	741	756	770	784	799	813	828	842
N.	L. 0	1	2	3	4	5	6	7	8	9

Proportional parts

	18	17	16	15	14
1	1.8	1.7	1.6	1.5	1.4
2	3.6	3.4	3.2	3.0	2.8
3	5.4	5.1	4.8	4.5	4.2
4	7.2	6.8	6.4	6.0	5.6
5	9.0	8.5	8.0	7.5	7.0
6	10.8	10.2	9.6	9.0	8.4
7	12.6	11.9	11.2	10.5	9.8
8	14.4	13.6	12.8	12.0	11.2
9	16.2	15.3	14.4	13.5	12.6

log e = 0.43429

Proportional parts

LOGARITHMS OF NUMBERS

300 — 350

N.	L.	0	1	2	3	4	5	6	7	8	9
300	47	712	727	741	756	770	784	799	813	828	842
301		857	871	885	900	914	929	943	958	972	986
302	48	001	015	029	044	058	073	087	101	116	130
303		144	159	173	187	202	216	230	244	259	273
304		287	302	316	330	344	359	373	387	401	416
305		430	444	458	473	487	501	515	530	544	558
306		572	586	601	615	629	643	657	671	686	700
307		714	728	742	756	770	785	799	813	827	841
308		855	869	883	897	911	926	940	954	968	982
309		996	*010	*024	*038	*052	*066	*080	*094	*108	*122
310	49	136	150	164	178	192	206	220	234	248	262
311		276	290	304	318	332	346	360	374	388	402
312		415	429	443	457	471	485	499	513	527	541
313		554	568	582	596	610	624	638	651	665	679
314		693	707	721	734	748	762	776	790	803	817
315		831	845	859	872	886	900	914	927	941	955
316		969	982	996	*010	*024	*037	*051	*065	*079	*092
317	50	106	120	133	147	161	174	188	202	215	229
318		243	256	270	284	297	311	325	338	352	365
319		379	393	406	420	433	447	461	474	488	501
320		515	529	542	556	569	583	596	610	623	637
321		651	664	678	691	705	718	732	745	759	772
322		786	799	813	826	840	853	866	880	893	907
323		920	934	947	961	974	987	*001	*014	*028	*041
324	51	055	068	081	095	108	121	135	148	162	175
325		188	202	215	228	242	255	268	282	295	308
326		322	335	348	362	375	388	402	415	428	441
327		455	468	481	495	508	521	534	548	561	574
328		587	601	614	627	640	654	667	680	693	706
329		720	733	746	759	772	786	799	812	825	838
330		851	865	878	891	904	917	930	943	957	970
331		983	996	*009	*022	*035	*048	*061	*075	*088	*101
332	52	114	127	140	153	168	179	192	205	218	231
333		244	257	270	284	297	310	323	336	349	362
334		375	388	401	414	427	440	453	466	479	492
335		504	517	530	543	556	569	582	595	608	621
336		634	647	660	673	686	699	711	724	737	750
337		763	776	789	802	815	827	840	853	866	879
338		892	905	917	930	943	956	969	982	994	*007
339	53	020	033	046	058	071	084	097	110	122	135
340		148	161	173	186	199	212	224	237	250	263
341		275	288	301	314	326	339	352	364	377	390
342		403	415	428	441	453	466	479	491	504	517
343		529	542	555	567	580	593	605	618	631	643
344		656	668	681	694	706	719	732	744	757	769
345		782	794	807	820	832	845	857	870	882	895
346		908	920	933	945	958	970	983	995	*008	*020
347	54	033	045	058	070	083	095	108	120	133	145
348		158	170	183	195	208	220	233	245	258	270
349		283	295	307	320	332	345	357	370	382	394
350		407	419	432	444	456	469	481	494	506	518
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	15	14	13	12
1	1.5	1.4	1.3	1.2
2	3.0	2.8	2.6	2.4
3	4.5	4.2	3.9	3.6
4	6.0	5.6	5.2	4.8
5	7.5	7.0	6.5	6.0
6	9.0	8.4	7.8	7.2
7	10.5	9.8	9.1	8.4
8	12.0	11.2	10.4	9.6
9	13.5	12.6	11.7	10.8

$\log \pi = 0.49715$

Proportional parts

47 712 — .54 518

350 — 400

N.	L.	0	1	2	3	4	5	6	7	8	9
350	54	407	419	432	444	456	469	481	494	506	518
351		531	543	555	568	580	593	605	617	630	642
352		654	667	679	691	704	716	728	741	753	765
353		777	790	802	814	827	839	851	864	876	888
354		900	913	925	937	949	962	974	986	998	*011
355	55	023	035	047	060	072	084	096	108	121	133
356		145	157	169	182	194	206	218	230	242	255
357		267	279	291	303	315	328	340	352	364	376
358		388	400	413	425	437	449	461	473	485	497
359		509	522	534	546	558	570	582	594	606	618
360		630	642	654	666	678	691	703	715	727	739
361		751	763	775	787	799	811	823	835	847	859
362		871	883	895	907	919	931	943	955	967	979
363		991	*003	*015	*027	*038	*050	*062	*074	*086	*098
364	56	110	122	134	146	158	170	182	194	205	217
365		229	241	253	265	277	289	301	312	324	336
366		348	360	372	384	396	407	419	431	443	455
367		467	478	490	502	514	526	538	549	561	573
368		585	597	608	620	632	644	656	667	679	691
369		703	714	726	738	750	761	773	785	797	808
370		820	832	844	855	867	879	891	902	914	926
371		937	949	961	972	984	996	*008	*019	*031	*043
372	57	054	066	078	089	101	113	124	136	148	159
373		171	183	194	206	217	229	241	252	264	276
374		287	299	310	322	334	345	357	368	380	392
375		403	415	426	438	449	461	473	484	496	507
376		519	530	542	553	565	576	588	600	611	623
377		634	646	657	669	680	692	703	715	726	738
378		749	761	772	784	795	807	818	830	841	852
379		864	875	887	898	910	921	933	944	955	967
380		978	990	*001	*013	*024	*035	*047	*058	*070	*081
381	58	092	104	115	127	138	149	161	172	184	195
382		206	218	229	240	252	263	274	286	297	309
383		320	331	343	354	365	377	388	399	410	422
384		433	444	456	467	478	490	501	512	524	535
385		546	557	569	580	591	602	614	625	636	647
386		659	670	681	692	704	715	726	737	749	760
387		771	782	794	805	816	827	838	850	861	872
388		883	894	906	917	928	939	950	961	973	984
389		995	*006	*017	*028	*040	*051	*062	*073	*084	*095
390	59	106	118	129	140	151	162	173	184	195	207
391		218	229	240	251	262	273	284	295	306	318
392		329	340	351	362	373	384	395	406	417	428
393		439	450	461	472	483	494	506	517	528	539
394		550	561	572	583	594	605	616	627	638	649
395		660	671	682	693	704	715	726	737	748	759
396		770	780	791	802	813	824	835	846	857	868
397		879	890	901	912	923	934	945	956	966	977
398		988	999	*010	*021	*032	*043	*054	*065	*076	*086
399	60	097	108	119	130	141	152	163	173	184	195
400		206	217	228	239	249	260	271	282	293	304
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	13	12	11	10
1	1.3	1.2	1.1	1.0
2	2.6	2.4	2.2	2.0
3	3.9	3.6	3.3	3.0
4	5.2	4.8	4.4	4.0
5	6.5	6.0	5.5	5.0
6	7.8	7.2	6.6	6.0
7	9.1	8.4	7.7	7.0
8	10.4	9.6	8.8	8.0
9	11.7	10.8	9.9	9.0

.54 407 — .60 304

N.	L.	0	1	2	3	4	5	6	7	8	9
400	60	206	217	228	239	249	260	271	282	293	304
401		314	325	336	347	358	369	379	390	401	412
402		423	433	444	455	466	477	487	498	509	520
403		531	541	552	563	574	584	595	606	617	627
404		638	649	660	670	681	692	703	713	724	735
405		746	756	767	778	788	799	810	821	831	842
406		853	863	874	885	895	906	917	927	938	949
407		959	970	981	991	*002	*013	*023	*034	*045	*055
408	61	066	077	087	098	109	119	130	140	151	162
409		172	183	194	204	215	225	236	247	257	268
410		278	289	300	310	321	331	342	352	363	374
411		384	395	405	416	426	437	448	458	469	479
412		490	500	511	521	532	542	553	563	574	584
413		595	606	616	627	637	648	658	669	679	690
414		700	711	721	731	742	752	763	773	784	794
415		805	815	826	836	847	857	868	878	888	899
416		909	920	930	941	951	962	972	982	993	*003
417	62	014	024	034	045	055	066	076	086	097	107
418		118	128	138	149	159	170	180	190	201	211
419		221	232	242	252	263	273	284	294	304	315
420		325	335	346	356	366	377	387	397	408	418
421		428	439	449	459	469	480	490	500	511	521
422		531	542	552	562	572	583	593	603	613	624
423		634	644	655	665	675	685	696	706	716	726
424		737	747	757	767	778	788	798	808	818	829
425		839	849	859	870	880	890	900	910	921	931
426		941	951	961	972	982	992	*002	*012	*022	*033
427	63	043	053	063	073	083	094	104	114	124	134
428		144	155	165	175	185	195	205	215	225	236
429		246	256	266	276	286	296	306	317	327	337
430		347	357	367	377	387	397	407	417	428	438
431		448	458	468	478	488	498	508	518	528	538
432		548	558	568	579	589	599	609	619	629	639
433		649	659	669	679	689	699	709	719	729	739
434		749	759	769	779	789	799	809	819	829	839
435		849	859	869	879	889	899	909	919	929	939
436		949	959	969	979	988	998	*008	*018	*028	*038
437	64	048	058	068	078	088	098	108	118	128	137
438		147	157	167	177	187	197	207	217	227	237
439		246	256	266	276	286	296	306	316	326	335
440		345	355	365	375	385	395	404	414	424	434
441		444	454	464	473	483	493	503	513	523	532
442		542	552	562	572	582	591	601	611	621	631
443		640	650	660	670	680	689	699	709	719	729
444		738	748	758	768	777	787	797	807	816	826
445		836	846	856	865	875	885	895	904	914	924
446		933	943	953	963	972	982	992	*002	*011	*021
447	65	031	040	050	060	070	079	089	099	108	118
448		128	137	147	157	167	176	186	196	205	215
449		225	234	244	254	263	273	283	292	302	312
450		321	331	341	350	360	369	379	389	398	408
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	11	10	9
1	1.1	1.0	0.9
2	2.2	2.0	1.8
3	3.3	3.0	2.7
4	4.4	4.0	3.6
5	5.5	5.0	4.5
6	6.6	6.0	5.4
7	7.7	7.0	6.3
8	8.8	8.0	7.2
9	9.9	9.0	8.1

Proportional parts

LOGARITHMS OF NUMBERS

450 — 500

N.	L.	0	1	2	3	4	5	6	7	8	9
450	65	321	331	341	350	360	369	379	389	398	408
451		418	427	437	447	456	466	475	485	495	504
452		514	523	533	543	552	562	571	581	591	600
453		610	619	629	639	648	658	667	677	686	696
454		706	715	725	734	744	753	763	772	782	792
455		801	811	820	830	839	849	858	868	877	887
456		896	906	916	925	935	944	954	963	973	982
457		992	*001	*011	*020	*030	*039	*049	*058	*068	*077
458	66	087	096	106	115	124	134	143	153	162	172
459		181	191	200	210	219	229	238	247	257	266
460		276	285	295	304	314	323	332	342	351	361
461		370	380	389	398	408	417	427	436	445	455
462		464	474	483	492	502	511	521	530	539	549
463		558	567	577	586	596	605	614	624	633	642
464		652	661	671	680	689	699	708	717	727	736
465		745	755	764	773	783	792	801	811	820	829
466		839	848	857	867	876	885	894	904	913	922
467		932	941	950	960	969	978	987	997	*006	*015
468	67	025	034	043	052	062	071	080	089	099	108
469		117	127	136	145	154	164	173	182	191	201
470		210	219	228	237	247	256	265	274	284	293
471		302	311	321	330	339	348	357	367	376	385
472		394	403	413	422	431	440	449	459	468	477
473		486	495	504	514	523	532	541	550	560	569
474		578	587	596	605	614	624	633	642	651	660
475		669	679	688	697	706	715	724	733	742	752
476		761	770	779	788	797	808	815	825	834	843
477		852	861	870	879	888	897	906	916	925	934
478		943	952	961	970	979	988	997	*006	*015	*024
479	68	034	043	052	061	070	079	088	097	106	115
480		124	133	142	151	160	169	178	187	196	205
481		215	224	233	242	251	260	269	278	287	296
482		305	314	323	332	341	350	359	368	377	386
483		395	404	413	422	431	440	449	458	467	476
484		485	494	502	511	520	529	538	547	556	565
485		574	583	592	601	610	619	628	637	646	655
486		664	673	681	690	699	708	717	726	735	744
487		753	762	771	780	789	797	806	815	824	833
488		842	851	860	869	878	886	895	904	913	922
489		931	940	949	958	966	975	984	993	*002	*011
490	89	020	028	037	046	055	064	073	082	090	099
491		108	117	126	135	144	152	161	170	179	188
492		197	205	214	223	232	241	249	258	267	276
493		285	294	302	311	320	329	338	346	355	364
494		373	381	390	399	408	417	425	434	443	452
495		461	469	478	487	496	504	513	522	531	539
496		548	557	566	574	583	592	601	609	618	627
497		636	644	653	662	671	679	688	697	705	714
498		723	732	740	749	758	767	775	784	793	801
499		810	819	827	836	845	854	862	871	880	888
500		897	906	914	923	932	940	949	958	966	975
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	10
1	1.0
2	2.0
3	3.0
4	4.0
5	5.0
6	6.0
7	7.0
8	8.0
9	9.0

	9
1	0.9
2	1.8
3	2.7
4	3.6
5	4.5
6	5.4
7	6.3
8	7.2
9	8.1

	8
1	0.8
2	1.6
3	2.4
4	3.2
5	4.0
6	4.8
7	5.6
8	6.4
9	7.2

Proportional parts

N.	L.	0	1	2	3	4	5	6	7	8	9
500	69	897	906	914	923	932	940	949	958	966	975
501		984	992	*001	*010	*018	*027	*036	*044	*053	*062
502	70	070	079	088	096	105	114	122	131	140	148
503		157	165	174	183	191	200	209	217	226	234
504		243	252	260	269	278	286	295	303	312	321
505		329	338	346	355	364	372	381	389	398	406
506		415	424	432	441	449	458	467	475	484	492
507		501	509	518	526	535	544	552	561	569	578
508		586	595	603	612	621	629	638	646	655	663
509		672	680	689	697	706	714	723	731	740	749
510		757	766	774	783	791	800	808	817	825	834
511		842	851	859	868	876	885	893	902	910	919
512		927	935	944	952	961	969	978	986	995	*003
513	71	012	020	029	037	046	054	063	071	079	088
514		096	105	113	122	130	139	147	155	164	172
515		181	189	198	206	214	223	231	240	248	257
516		265	273	282	290	299	307	315	324	332	341
517		349	357	366	374	383	391	399	408	416	425
518		433	441	450	458	466	475	483	492	500	508
519		517	525	533	542	550	559	567	575	584	592
520		600	609	617	625	634	642	650	659	667	675
521		684	692	700	709	717	725	734	742	750	759
522		767	775	784	792	800	809	817	825	834	842
523		850	858	867	875	883	892	900	908	917	925
524		933	941	950	958	966	975	983	991	999	*008
525	72	016	024	032	041	049	057	066	074	082	090
526		099	107	115	123	132	140	148	156	165	173
527		181	189	198	206	214	222	230	239	247	255
528		263	272	280	288	296	304	313	321	329	337
529		346	354	362	370	378	387	395	403	411	419
530		428	436	444	452	460	469	477	485	493	501
531		509	518	526	634	542	550	558	567	575	583
532		591	599	607	616	624	632	640	648	656	665
533		673	681	689	697	705	713	722	730	738	746
534		754	762	770	779	787	795	803	811	819	827
535		835	843	852	860	868	876	884	892	900	908
536		916	925	933	941	949	957	965	973	981	989
537		997	*006	*014	*022	*030	*038	*046	*054	*062	*070
538	73	078	086	094	102	111	119	127	135	143	151
539		159	167	175	183	191	199	207	215	223	231
540		239	247	255	263	272	280	288	296	304	312
541		320	328	336	344	352	360	368	376	384	392
542		400	408	416	424	432	440	448	456	464	472
543		480	488	496	504	512	520	528	536	544	552
544		560	568	576	584	592	600	608	616	624	632
545		640	648	656	664	672	679	687	695	703	711
546		719	727	735	743	751	759	767	775	783	791
547		799	807	815	823	830	838	846	854	862	870
548		878	886	894	902	910	918	926	933	941	949
549		957	965	973	981	989	997	*005	*013	*020	*028
550	74	036	044	052	060	068	076	084	092	099	107
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	9
1	0.9
2	1.8
3	2.7
4	3.6
5	4.5
6	5.4
7	6.3
8	7.2
9	8.1

	8
1	0.8
2	1.6
3	2.4
4	3.2
5	4.0
6	4.8
7	5.6
8	6.4
9	7.2

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

Proportional parts

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
550	74	036	044	052	060	068	076	084	092	099	107	
551		115	123	131	139	147	155	162	170	178	186	
552		194	202	210	218	225	233	241	249	257	265	
553		273	280	288	296	304	312	320	327	335	343	
554		351	359	367	374	382	390	398	406	414	421	
555		429	437	445	453	461	468	476	484	492	500	
556		507	515	523	531	539	547	554	562	570	578	
557		586	593	601	609	617	624	632	640	648	656	
558		663	671	679	687	695	702	710	718	726	733	
559		741	749	757	764	772	780	788	796	803	811	
560		819	827	834	842	850	858	865	873	881	889	
561		896	904	912	920	927	935	943	950	958	966	
562		974	981	989	997	*005	*012	*020	*028	*035	*043	
563	75	051	059	066	074	082	089	097	105	113	120	
564		128	136	143	151	159	166	174	182	189	197	
565		205	213	220	228	236	243	251	259	266	274	
566		282	289	297	305	312	320	328	335	343	351	
567		358	366	374	381	389	397	404	412	420	427	
568		435	442	450	458	465	473	481	488	496	504	
569		511	519	526	534	542	549	557	565	572	580	
570		587	595	603	610	618	626	633	641	648	656	
571		664	671	679	686	694	702	709	717	724	732	
572		740	747	755	762	770	778	785	793	800	808	
573		815	823	831	838	846	853	861	868	876	884	
574		891	899	906	914	921	929	937	944	952	959	
575		967	974	982	989	997	*005	*012	*020	*027	*035	
576	76	042	050	057	065	072	080	087	095	103	110	
577		118	125	133	140	148	155	163	170	178	185	
578		193	200	208	215	223	230	238	245	253	260	
579		268	275	283	290	298	305	313	320	328	335	
580		343	350	358	365	373	380	388	395	403	410	
581		418	425	433	440	448	455	462	470	477	485	
582		492	500	507	515	522	530	537	545	552	559	
583		567	574	582	589	597	604	612	619	626	634	
584		641	649	656	664	671	678	686	693	701	708	
585		716	723	730	738	745	753	760	768	775	782	
586		790	797	805	812	819	827	834	842	849	856	
587		864	871	879	886	893	901	908	916	923	930	
588		938	945	953	960	967	975	982	989	997	*004	
589	77	012	019	026	034	041	048	056	063	070	078	
590		085	093	100	107	115	122	129	137	144	151	
591		159	166	173	181	188	195	203	210	217	225	
592		232	240	247	254	262	269	276	283	291	298	
593		305	313	320	327	335	342	349	357	364	371	
594		379	386	393	401	408	415	422	430	437	444	
595		452	459	466	474	481	488	495	503	510	517	
596		525	532	539	546	554	561	568	576	583	590	
597		597	605	612	619	627	634	641	648	656	663	
598		670	677	685	692	699	706	714	721	728	735	
599		743	750	757	764	772	779	786	793	801	808	
600	—	815	822	830	837	844	851	859	866	873	880	
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

Proportional parts:

	8
1	0.8
2	1.6
3	2.4
4	3.2
5	4.0
6	4.8
7	5.6
8	6.4
9	7.2

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

N.	L.	0	1	2	3	4	5	6	7	8	9
600	77	815	822	830	837	844	851	859	866	873	880
601		887	895	902	909	916	924	931	938	945	952
602		960	967	974	981	988	996	*003	*010	*017	*025
603	78	032	039	046	053	061	068	075	082	089	097
604		104	111	118	125	132	140	147	154	161	168
605		176	183	190	197	204	211	219	226	233	240
606		247	254	262	269	276	283	290	297	305	312
607		319	326	333	340	347	355	362	369	376	383
608		390	398	405	412	419	426	433	440	447	455
609		462	469	476	483	490	497	504	512	519	526
610		533	540	547	554	561	569	576	583	590	597
611		604	611	618	625	633	640	647	654	661	668
612		675	682	689	696	704	711	718	725	732	739
813		746	753	760	767	774	781	789	796	803	810
614		817	824	831	838	845	852	859	866	873	880
615		888	895	902	909	916	923	930	937	944	951
616		958	965	972	979	986	993	*000	*007	*014	*021
617	79	029	036	043	050	057	064	071	078	085	092
618		099	106	113	120	127	134	141	148	155	162
619		169	176	183	190	197	204	211	218	225	232
620		239	246	253	260	267	274	281	288	295	302
621		309	316	323	330	337	344	351	358	365	372
622		379	386	393	400	407	414	421	428	435	442
623		449	456	483	470	477	484	491	498	505	511
624		518	525	532	539	546	553	560	567	574	581
625		588	595	602	609	616	623	630	637	644	650
626		657	684	671	678	685	692	699	706	713	720
627		727	734	741	748	754	761	768	775	782	789
628		796	803	810	817	824	831	837	844	851	858
629		865	872	879	886	893	900	906	913	920	927
630		934	941	948	955	962	969	975	982	989	996
631	80	003	010	017	024	030	037	044	051	058	065
632		072	079	085	092	099	106	113	120	127	134
633		140	147	154	161	168	175	182	188	195	202
634		209	216	223	229	236	243	250	257	264	271
635		277	284	291	298	305	312	318	325	332	339
636		346	353	359	366	373	380	387	393	400	407
637		414	421	428	434	441	448	455	462	468	475
638		482	489	496	502	509	516	523	530	536	543
639		550	557	564	570	577	584	591	598	604	611
640		618	625	632	638	645	652	659	665	672	679
641		686	693	699	706	713	720	726	733	740	747
642		754	760	787	774	781	787	794	801	808	814
643		821	828	835	841	848	855	862	868	875	882
644		889	895	902	909	916	922	929	936	943	949
645		956	963	969	976	983	990	996	*003	*010	*017
646	81	023	030	037	043	050	057	064	070	077	084
647		090	097	104	111	117	124	131	137	144	151
648		158	164	171	178	184	191	198	204	211	218
649		224	231	238	245	251	258	265	271	278	285
650		291	298	305	311	318	325	331	338	345	351
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	8
1	0.8
2	1.6
3	2.4
4	3.2
5	4.0
6	4.8
7	5.6
8	6.4
9	7.2

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

Proportional parts

LOGARITHMS OF NUMBERS

650 — 700

N.	L.	0	1	2	3	4	5	6	7	8	9
650	81	291	298	305	311	318	325	331	338	345	351
651		358	365	371	378	385	391	398	405	411	418
652		425	431	438	445	451	458	465	471	478	485
653		491	498	505	511	518	525	531	538	544	551
654		558	564	571	578	584	591	598	604	611	617
855		624	631	637	644	651	657	664	671	677	684
656		690	697	704	710	717	723	730	737	743	750
657		757	763	770	776	783	790	796	803	809	816
658		823	829	836	842	849	856	862	869	875	882
659		889	895	902	908	915	921	928	935	941	948
660		954	961	968	974	981	987	994	*000	*007	*014
661	82	020	027	033	040	046	053	060	066	073	079
662		086	092	099	105	112	119	125	132	138	145
663		151	158	164	171	178	184	191	197	204	210
664		217	223	230	236	243	249	256	263	269	276
665		282	289	295	302	308	315	321	328	334	341
666		347	354	360	367	373	380	387	393	400	406
667		413	419	426	432	439	445	452	458	465	471
668		478	484	491	497	504	510	517	523	530	536
669		543	549	556	562	569	575	582	588	595	601
670		607	614	620	627	633	640	646	653	659	666
671		672	679	685	692	698	705	711	718	724	730
672		737	743	750	756	763	769	776	782	789	795
673		802	808	814	821	827	834	840	847	853	860
674		866	872	879	885	892	898	905	911	918	924
675		930	937	943	950	956	963	969	975	982	988
676		995	*001	*008	*014	*020	*027	*033	*040	*046	*052
677	83	059	065	072	078	085	091	097	104	110	117
678		123	129	136	142	149	155	161	168	174	181
679		187	193	200	206	213	219	225	232	238	245
680		251	257	264	270	276	283	289	296	302	308
681		315	321	327	334	340	347	353	359	366	372
682		378	385	391	398	404	410	417	423	429	436
683		442	448	455	461	467	474	480	487	493	499
684		506	512	518	525	531	537	544	550	556	563
685		569	575	582	588	594	601	607	613	620	626
686		632	639	645	651	658	664	670	677	683	689
687		696	702	708	715	721	727	734	740	746	753
688		759	765	771	778	784	790	797	803	809	816
689		822	828	835	841	847	853	860	866	872	879
690		885	891	897	904	910	916	923	929	935	942
691		948	954	960	967	973	979	985	992	998	*004
692	84	011	017	023	029	036	042	048	055	061	067
693		073	080	086	092	098	105	111	117	123	130
694		136	142	148	155	161	167	173	180	186	192
695		198	205	211	217	223	230	236	242	248	255
696		261	267	273	280	286	292	298	305	311	317
697		323	330	336	342	348	354	361	367	373	379
698		386	392	398	404	410	417	423	429	435	442
699		448	454	460	466	473	479	485	491	497	504
700		510	516	522	528	535	541	547	553	559	566
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

Proportional parts

N.	L.	0	1	2	3	4	5	6	7	8	9
700	84	510	516	522	528	535	541	547	553	559	566
701		572	578	584	590	597	603	609	615	621	628
702		634	640	646	652	658	665	671	677	683	689
703		696	702	708	714	720	726	733	739	745	751
704		757	763	770	776	782	788	794	800	807	813
705		819	825	831	837	844	850	856	862	868	874
706		880	887	893	899	905	911	917	924	930	936
707		942	948	954	960	967	973	979	985	991	997
708	85	003	009	016	022	028	034	040	046	052	058
709		065	071	077	083	089	095	101	107	114	120
710		126	132	138	144	150	156	163	169	175	181
711		187	193	199	205	211	217	224	230	236	242
712		248	254	260	266	272	278	285	291	297	303
713		309	315	321	327	333	339	345	352	358	364
714		370	376	382	388	394	400	406	412	418	425
715		431	437	443	449	455	461	467	473	479	485
716		491	497	503	509	516	522	528	534	540	546
717		552	558	564	570	576	582	588	594	600	606
718		612	618	625	631	637	643	649	655	661	667
719		673	679	685	691	697	703	709	715	721	727
720		733	739	745	751	757	763	769	775	781	788
721		794	800	806	812	818	824	830	836	842	848
722		854	860	866	872	878	884	890	896	902	908
723		914	920	926	932	938	944	950	956	962	968
724		974	980	986	992	998	*004	*010	*016	*022	*028
725	86	034	040	046	052	058	064	070	076	082	088
726		094	100	106	112	118	124	130	136	141	147
727		153	159	165	171	177	183	189	195	201	207
728		213	219	225	231	237	243	249	255	261	267
729		273	279	285	291	297	303	308	314	320	326
730		332	338	344	350	356	362	368	374	380	386
731		392	398	404	410	415	421	427	433	439	445
732		451	457	463	469	475	481	487	493	499	504
733		510	516	522	528	534	540	546	552	558	564
734		570	576	581	587	593	599	605	611	617	623
735		629	635	641	646	652	658	664	670	676	682
736		688	694	700	705	711	717	723	729	735	741
737		747	753	759	764	770	776	782	788	794	800
738		806	812	817	823	829	835	841	847	853	859
739		864	870	876	882	888	894	900	906	911	917
740		923	929	935	941	947	953	958	964	970	976
741		982	988	994	999	*005	*011	*017	*023	*029	*035
742	87	040	046	052	058	064	070	075	081	087	093
743		099	105	111	116	122	128	134	140	146	151
744		157	163	169	175	181	186	192	198	204	210
745		216	221	227	233	239	245	251	256	262	268
746		274	280	286	291	297	303	309	315	320	326
747		332	338	344	349	355	361	367	373	379	384
748		390	396	402	408	413	419	425	431	437	442
749		448	454	460	466	471	477	483	489	495	500
750		506	512	518	523	529	535	541	547	552	558
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

	5
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5

Proportional parts

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
750	87	506	512	518	523	529	535	541	547	552	558	
751		564	570	576	581	587	593	599	604	610	616	
752		622	628	633	639	645	651	656	662	668	674	
753		679	685	691	697	703	708	714	720	726	731	
754		737	743	749	754	760	766	772	777	783	789	
755		795	800	806	812	818	823	829	835	841	846	
756		852	858	864	869	875	881	887	892	898	904	
757		910	915	921	927	933	938	944	950	955	961	
758		967	973	978	984	990	996	*001	*007	*013	*018	
759	88	024	030	036	041	047	053	058	064	070	076	
760		081	087	093	098	104	110	116	121	127	133	6
761		138	144	150	156	161	167	173	178	184	190	1 0.6
762		195	201	207	213	218	224	230	235	241	247	2 1.2
763		252	258	264	270	275	281	287	292	298	304	3 1.8
764		309	315	321	326	332	338	343	349	355	360	4 2.4
765		366	372	377	383	389	395	400	406	412	417	5 3.0
766		423	429	434	440	446	451	457	463	468	474	6 3.6
767		480	485	491	497	502	508	513	519	525	530	7 4.2
768		536	542	547	553	559	564	570	576	581	587	8 4.8
769		593	598	604	610	615	621	627	632	638	643	9 5.4
770		649	655	660	666	672	677	683	689	694	700	
771		705	711	717	722	728	734	739	745	750	756	
772		762	767	773	779	784	790	795	801	807	812	
773		818	824	829	835	840	846	852	857	863	868	
774		874	880	885	891	897	902	908	913	919	925	
775		930	936	941	947	953	958	964	969	975	981	
776		986	992	997	*003	*009	*014	*020	*025	*031	*037	
777	89	042	048	053	059	064	070	076	081	087	092	
778		098	104	109	115	120	126	131	137	143	148	
779		154	159	165	170	176	182	187	193	198	204	
780		209	215	221	226	232	237	243	248	254	260	5
781		265	271	276	282	287	293	298	304	310	315	1 0.5
782		321	326	332	337	343	348	354	360	365	371	2 1.0
783		376	382	387	393	398	404	409	415	421	426	3 1.5
784		432	437	443	448	454	459	465	470	476	481	4 2.0
785		487	492	498	504	509	515	520	526	531	537	5 2.5
786		542	548	553	559	564	570	575	581	586	592	6 3.0
787		597	603	609	614	620	625	631	636	642	647	7 3.5
788		653	658	664	669	675	680	686	691	697	702	8 4.0
789		708	713	719	724	730	735	741	746	752	757	9 4.5
790		763	768	774	779	785	790	796	801	807	812	
791		818	823	829	834	840	845	851	856	862	867	
792		873	878	883	889	894	900	905	911	916	922	
793		927	933	938	944	949	955	960	966	971	977	
794		982	988	993	998	*004	*009	*015	*020	*026	*031	
795	90	037	042	048	053	059	064	069	075	080	086	
796		091	097	102	108	113	119	124	129	135	140	
797		146	151	157	162	168	173	179	184	189	195	
798		200	206	211	217	222	227	233	238	244	249	
799		255	260	266	271	276	282	287	293	298	304	
800		309	314	320	325	331	336	342	347	352	358	
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

N.	L.	0	1	2	3	4	5	6	7	8	9
800	90	309	314	320	325	331	336	342	347	352	358
801		363	369	374	380	385	390	396	401	407	412
802		417	423	428	434	439	445	450	455	461	466
803		472	477	482	488	493	499	504	509	515	520
804		526	531	536	542	547	553	558	563	569	574
805		580	585	590	596	601	607	612	617	623	628
806		634	639	644	650	655	660	666	671	677	882
807		687	693	698	703	709	714	720	725	730	736
808		741	747	752	757	763	768	773	779	784	789
809		795	800	806	811	816	822	827	832	838	843
810		849	854	859	865	870	875	881	886	891	897
811		902	907	913	918	924	929	934	940	945	950
812		956	961	966	972	977	982	988	993	998	*004
813	91	009	014	020	025	030	036	041	046	052	057
814		062	068	073	078	084	089	094	100	105	110
815		116	121	126	132	137	142	148	153	158	164
816		169	174	180	185	190	196	201	206	212	217
817		222	228	233	238	243	249	254	259	265	270
818		275	281	286	291	297	302	307	312	318	323
819		328	334	339	344	350	355	360	365	371	376
820		381	387	392	397	403	408	413	418	424	429
821		434	440	445	450	455	461	466	471	477	482
822		487	492	498	503	503	514	519	524	529	535
823		540	545	551	556	561	566	572	577	582	587
824		593	598	603	609	614	619	624	630	635	640
825		645	651	656	661	666	672	677	682	687	693
826		698	703	709	714	719	724	730	735	740	745
827		751	756	761	766	772	777	782	787	793	798
828		803	808	814	819	824	829	834	840	845	850
829		855	861	866	871	876	882	887	892	897	903
830		908	913	918	924	929	934	939	944	950	955
831		960	965	971	976	981	986	991	997	*002	*007
832	92	012	018	023	028	033	038	044	049	054	059
833		065	070	075	080	035	091	096	101	106	111
834		117	122	127	132	137	143	148	153	153	163
835		169	174	179	184	189	195	200	205	210	215
836		221	226	231	236	241	247	252	257	262	267
837		273	278	283	288	293	298	304	309	314	319
838		324	330	335	340	345	350	355	361	366	371
839		376	381	387	392	397	402	407	412	418	423
840		428	433	438	443	449	454	459	464	469	474
841		480	485	490	495	500	505	511	516	521	526
842		531	536	542	547	552	557	562	567	572	578
843		583	588	593	598	603	609	614	619	624	629
844		634	639	645	650	655	660	665	670	675	681
845		686	691	696	701	706	711	716	722	727	732
846		737	742	747	752	758	763	768	773	778	783
847		788	793	799	804	809	814	819	824	829	834
848		840	845	850	855	860	865	870	875	881	886
849		891	896	901	906	911	916	921	927	932	937
850		942	947	952	957	962	967	973	978	983	988
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

	5
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5

Proportional parts

N.	L.	0	1	2	3	4	5	6	7	8	9
850	92	942	947	952	957	962	967	973	978	983	988
851		993	998	*003	*008	*013	*018	*024	*029	*034	*039
852	93	044	049	054	059	064	069	075	080	085	090
853		095	100	105	110	115	120	125	131	136	141
854		146	151	156	161	166	171	176	181	186	192
855		197	202	207	212	217	222	227	232	237	242
856		247	252	258	263	268	273	278	283	288	293
857		298	303	308	313	318	323	328	334	339	344
858		349	354	359	364	369	374	379	384	389	394
859		399	404	409	414	420	425	430	435	440	445
860		450	455	460	465	470	475	480	485	490	495
861		500	505	510	515	520	526	531	536	541	546
862		551	556	561	566	571	576	581	586	591	596
863		601	606	611	616	621	626	631	636	641	646
864		651	656	661	666	671	676	682	687	692	697
865		702	707	712	717	722	727	732	737	742	747
866		752	757	762	767	772	777	782	787	792	797
867		802	807	812	817	822	827	832	837	842	847
868		852	857	862	867	872	877	882	887	892	897
869		902	907	912	917	922	927	932	937	942	947
870		952	957	962	967	972	977	982	987	992	997
871	94	002	007	012	017	022	027	032	037	042	047
872		052	057	062	067	072	077	082	086	091	096
873		101	106	111	116	121	126	131	136	141	146
874		151	156	161	166	171	176	181	186	191	196
875		201	206	211	216	221	226	231	236	240	245
876		250	255	260	265	270	275	280	285	290	295
877		300	305	310	315	320	325	330	335	340	345
878		349	354	359	364	369	374	379	384	389	394
879		399	404	409	414	419	424	429	433	438	443
880		448	453	458	463	468	473	478	483	488	493
881		498	503	507	512	517	522	527	532	537	542
882		547	552	557	562	567	571	576	581	586	591
883		596	601	606	611	616	621	626	630	635	640
884		645	650	655	660	665	670	675	680	685	689
885		694	699	704	709	714	719	724	729	734	738
886		743	748	753	758	763	768	773	778	783	787
887		792	797	802	807	812	817	822	827	832	836
888		841	846	851	856	861	866	871	876	880	885
889		890	895	900	905	910	915	919	924	929	934
890		939	944	949	954	959	963	968	973	978	983
891		988	993	998	*002	*007	*012	*017	*022	*027	*032
892	95	036	041	046	051	056	061	066	071	075	080
893		085	090	095	100	105	109	114	119	124	129
894		134	139	143	148	153	158	163	168	173	177
895		182	187	192	197	202	207	211	216	221	226
896		231	236	240	245	250	255	260	265	270	274
897		279	284	289	294	299	303	308	313	318	323
898		328	332	337	342	347	352	357	361	366	371
899		376	381	386	390	395	400	405	410	415	419
900		424	429	434	439	444	448	453	458	463	468
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

	5
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5

	4
1	0.4
2	0.8
3	1.2
4	1.6
5	2.0
6	2.4
7	2.8
8	3.2
9	3.6

Proportional parts

LOGARITHMS OF NUMBERS

900 — 950

N.	L.	0	1	2	3	4	5	6	7	8	9
900	95	424	429	434	439	444	448	453	458	463	468
901		472	477	482	487	492	497	501	506	511	516
902		521	525	530	535	540	545	550	554	559	564
903		569	574	578	583	588	593	598	602	607	612
904		617	622	626	631	636	641	646	650	655	660
905		665	670	674	679	684	689	694	698	703	708
906		713	718	722	727	732	737	742	746	751	756
907		761	766	770	775	780	785	789	794	799	804
908		809	813	818	823	828	832	837	842	847	852
909		856	861	866	871	875	880	885	890	895	899
910		904	909	914	918	923	928	933	938	942	947
911		952	957	961	966	971	976	980	985	990	995
912		999	*004	*009	*014	*019	*023	*028	*033	*038	*042
913	96	047	052	057	061	066	071	076	080	085	090
914		095	099	104	109	114	118	123	128	133	137
915		142	147	152	156	161	166	171	175	180	185
916		190	194	199	204	209	213	218	223	227	232
917		237	242	246	251	256	261	265	270	275	280
918		284	289	294	298	303	308	313	317	322	327
919		332	336	341	346	350	355	360	365	369	374
920		379	384	388	393	398	402	407	412	417	421
921		426	431	435	440	445	450	454	459	464	468
922		473	478	483	487	492	497	501	506	511	515
923		520	525	530	534	539	544	548	553	558	562
924		567	572	577	581	586	591	595	600	605	609
925		614	619	624	628	633	638	642	647	652	656
926		661	666	670	675	680	685	689	694	699	703
927		708	713	717	722	727	731	736	741	745	750
928		755	759	764	769	774	778	783	788	792	797
929		802	806	811	816	820	825	830	834	839	844
930		848	853	858	862	867	872	876	881	886	890
931		895	900	904	909	914	918	923	928	932	937
932		942	946	951	956	960	965	970	974	979	984
933		988	993	997	*002	*007	*011	*016	*021	*025	*030
934	97	035	039	044	049	053	058	063	067	072	077
935		081	086	090	095	100	104	109	114	118	123
936		128	132	137	142	146	151	155	160	165	169
937		174	179	183	188	192	197	202	206	211	216
938		220	225	230	234	239	243	248	253	257	262
939		267	271	276	280	285	290	294	299	304	308
940		313	317	322	327	331	336	340	345	350	354
941		359	364	368	373	377	382	387	391	396	400
942		405	410	414	419	424	428	433	437	442	447
943		451	456	460	465	470	474	479	483	488	493
944		497	502	506	511	516	520	525	529	534	539
945		543	548	552	557	562	566	571	575	580	585
946		589	594	598	603	607	612	617	621	626	630
947		635	640	644	649	653	658	663	667	672	676
948		681	685	690	695	699	704	708	713	717	722
949		727	731	736	740	745	749	754	759	763	768
950		772	777	782	786	791	795	800	804	809	813
N.	L.	0	1	2	3	4	5	6	7	8	9

Proportional parts

	5
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5

	4
1	0.4
2	0.8
3	1.2
4	1.6
5	2.0
6	2.4
7	2.8
8	3.2
9	3.6

Proportional parts

LOGARITHMS OF NUMBERS

950 — 1000

N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts
950	97	772	777	782	786	791	795	800	804	809	813	
951		818	823	827	832	836	841	845	850	855	859	
952		864	868	873	877	882	886	891	896	900	905	
963		909	914	918	923	928	932	937	941	946	950	
954		955	959	964	968	973	978	982	987	991	996	
955	98	000	005	009	014	019	023	028	032	037	041	
956		046	050	055	059	064	068	073	078	082	087	
957		091	096	100	105	109	114	118	123	127	132	
958		137	141	146	150	155	159	164	168	173	177	
959		182	186	191	195	200	204	209	214	218	223	
960		227	232	236	241	245	250	254	259	263	268	5
961		272	277	281	286	290	295	299	304	308	313	1 0.5
962		318	322	327	331	336	340	345	349	354	358	2 1.0
963		363	367	372	376	381	385	390	394	399	403	3 1.5
964		408	412	417	421	426	430	435	439	444	448	4 2.0
965		453	457	462	466	471	475	480	484	489	493	5 2.5
966		498	502	507	511	516	520	525	529	534	538	6 3.0
967		543	547	552	556	561	565	570	574	579	583	7 3.5
968		588	592	597	601	605	610	614	619	623	628	8 4.0
969		632	637	641	646	650	655	659	664	668	673	9 4.5
970		677	682	686	691	695	700	704	709	713	717	
971		722	726	731	735	740	744	749	753	758	762	
972		767	771	776	780	784	789	793	798	802	807	
973		811	816	820	825	829	834	838	843	847	851	
974		856	860	865	869	874	878	883	887	892	896	
975		900	905	909	914	918	923	927	932	936	941	
976		945	949	954	958	963	967	972	976	981	985	
977		989	994	998	*003	*007	*012	*016	*021	*025	*029	
978	99	034	038	043	047	052	056	061	065	069	074	
979		078	083	087	092	096	100	105	109	114	118	
980		123	127	131	136	140	145	149	164	158	162	4
981		167	171	176	180	185	189	193	198	202	207	1 0.4
982		211	216	220	224	229	233	238	242	247	251	2 0.8
983		255	260	264	269	273	277	282	286	291	295	3 1.2
984		300	304	308	313	317	322	326	330	335	339	4 1.6
985		344	348	352	357	361	366	370	374	379	383	5 2.0
986		388	392	396	401	405	410	414	419	423	427	6 2.4
987		432	436	441	445	449	454	458	463	467	471	7 2.8
988		476	480	484	489	493	498	502	506	511	515	8 3.2
989		520	524	528	533	537	542	546	550	555	559	9 3.6
990		564	568	572	577	581	585	590	594	599	603	
991		607	612	616	621	625	629	634	638	642	647	
992		651	656	660	664	669	673	677	682	686	691	
993		695	699	704	708	712	717	721	726	730	734	
994		739	743	747	752	756	760	765	769	774	778	
995		782	787	791	795	800	804	808	813	817	822	
996		826	830	835	839	843	848	852	856	861	865	
997		870	874	878	883	887	891	896	900	904	909	
998		913	917	922	926	930	935	939	944	948	952	
999		957	961	965	970	974	978	983	987	991	996	
1000	00	000	004	009	013	017	022	026	030	035	039	
N.	L.	0	1	2	3	4	5	6	7	8	9	Proportional parts

INTERNATIONAL ATOMIC WEIGHTS 1941

	Symbol	Atomic No.	Atomic Weight		Symbol	Atomic No.	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

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